

BOSTON UNIVERSITY GRADUATE SCHOOL

~~Dissertation~~
~~thesis~~

TITANIC HYDRIDE AS A
REDUCING AGENT

by

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requirements for the degree of
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Approved

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Instructor



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The author wishes to thank Dr. Chester M. Alter for suggesting this problem, and for his helpful advice in working it out. Also, I wish to thank both Dr. Chester M. Alter and Dr. Lowell V. Coulter for reading and suggesting alterations in this research.

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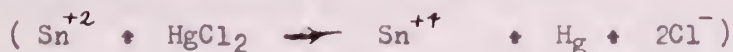
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CHAPTER I

A BRIEF REVIEW OF THE VOLUMETRIC PROCEDURES FOR IRON AND COMPOUNDS COMMONLY OCCURRING WITH IRON. EMPHASIS PLACED ON THE REDUCTION PROCESSES.

To students of chemistry, probably the most common method of reducing iron is the use of a freshly prepared stannous chloride solution. The reduction of iron by stannous chloride, however, often leads to the formation of metallic mercury, unless care is taken not to add more than a slight excess (one to two drops) of the chloride.



The appearance of a gray or black precipitate of mercury is the sign to discard the sample and start over again. The presence of much mercurous chloride in the solution may cause error, because permanganate may be oxidized by it. Also, the end point of permanganate can be very indistinct under certain conditions. Too much sulfuric acid or mercurous chloride (which can be oxidized by permanganate or ferric ion) and the presence of manganous ions all tend to result in a fading end point.

The reaction of Mn^{+2} with permanganate is very slow in cold acid solution.



It is advisable to remove all chloride ion, since the reaction between permanganate and ferrous iron induces a reaction between permanganate and hydrochloric acid, whereby a part of the chloride is oxidized to hypochlorous acid. Unfortunately, the hypochlorous acid reacts only slowly with ferrous ion, with the result that the error is not balanced

out, and too much permanganate is used. The explanation of this induced reaction lies in the fact that the oxidation of ferrous iron produces an intermediate form of iron in a higher state of oxidation than ferric iron. The higher oxidation form of iron is very unstable, and reacts extremely rapidly with ferrous ions to form ferric ions. In the presence of hydrochloric acid, some of the super-oxidized iron reacts with chloride ion to form chlorine, which hydrolyzes to form HClO , hypochlorous acid. The addition of manganous salt (Zimmerman-Reinhardt solution) prevents this induced reaction. It is assumed that the manganese reacts with the super-oxidized iron to form tri- or quadrivalent manganese, which then reacts immediately with ferrous iron. Thus the oxidation of the chloride is reduced to a minimum. The effect of hydrochloric acid discussed above must be considered in all permanganate titrations, regardless of the method of reduction. In titrations with dichromate and ceric sulfate, the presence of chloride can be ignored if the concentration of the latter is less than 1 N.

Thus far we have mentioned only stannous chloride as a reducing agent for iron. A variation in this method of reduction is the method of Fresenius¹, in which the excess stannous chloride, instead of being destroyed by an excess of mercurous chloride, is determined by iodine titration. Special precautions must be taken to obtain accurate results. In the course of this research, methylene blue was tried as an oxidation-reduction indicator for the end point of the stannous chloride oxidation. The color change, however, was very gradual. Probably this

1 Z. Anal. Chem., Volume 1, Number 26. 1862.

was caused by the fact that the oxidation potentials of the methylene white-methylene blue and stannous-stannic systems were not too close together. In normal acid, the methylene white-methylene blue system has an oxidation potential of 175-350 millivolts, according to the value of the ratio $\frac{\text{oxidation}}{\text{reduction}}$, while the stannous-stannic system in normal acid is about 150 millivolts. Under proper conditions, a sharp color change might be obtained.

The use of silicomolybdic acid indicator before the volumetric oxidation of iron is described by Titus and Sill¹. The silicomolybdic acid indicator is reduced to molybdenum blue by stannous chloride. The molybdenum blue color disappears just before the oxidation of the ferrous ion begins. Potassium dichromate was used as the standard oxidizing solution, and the iron was reduced, as usual, with stannous chloride. N-phenyl-anthranilic acid indicator was used for the ferrous end point. An accuracy of one part per thousand was obtained. One disadvantage in this determination of iron is the necessity of boiling the solution in sulfuric acid (20 ml. conc./200) for twenty minutes after the stannous chloride end point has been obtained, in order to destroy the silicomolybdic acid indicator. If the silicomolybdic acid indicator is not destroyed, it causes a muddy brown color at the second end point. The solution was cooled for six minutes. Thus, for the danger involved in using mercurous chloride is substituted the danger of boiling the ferrous iron solution, after the stannous chloride has

¹ Titus, Albert C. and Claude W. Sill, "Use of Silicomolybdic Acid Indicator before the Volumetric Oxidation of Iron," Industrial and Engineering Chemistry, Analytical Edition, Volume 13, pages 416-418. 1941.

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been oxidized, for twenty minutes in hot sulfuric acid solution. Also, approximately one half hour is added to the time of the determination. The authors, however, claim that the air oxidation was such that in twenty minutes it would amount to over 0.1 ml. with no watch glass in place. In a later article¹, the same procedure is used, with the substitution of ceric sulfate for potassium dichromate and O-phenylanthranilic acid for the second indicator. Silicomolybdic acid indicator of Titus and Sill was used in this research in an attempt to indicate the titanium end point of the titration. It was found, however, that this indicator was not practicable, since the color change was very gradual and in many cases the indicator turned brownish-yellow when it was not added close enough to the end point. Heating and the use of sulfuric or hydrochloric acid all failed to improve the end point.

Another widely applied method used in the reduction of iron is the use of various metals or metallic amalgams. Care must be taken while interpreting results in the presence of titanium, vanadium, chromium, molybdenum, and other reducible ions, since they are usually reduced with the iron, causing high results.

Table 1 shows the effect of various reducing agents on iron in the presence of other metals commonly occurring in its ores. Hydrogen sulfide, sulphur dioxide, and hydrogen with a platinum catalyst are seldom applied because they are tedious in application, requiring an hour or more to complete the reduction process. The metals used for reduction

¹ Titus, Albert C. and Claude W. Sill, "Ceric Sulfate in Determination of Iron Using Molybdisilic (Silicomolybdic) Acid Method." Ind. and Eng. Chem., Anal. Ed., Volume 14, Number 121. 1942.

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must be iron-free, or sizeable blanks must be subtracted. Also, their use requires special apparatus which is time-consuming. There is no way of knowing when the reduction process is complete, because dilute solutions of ferric ion are almost colorless.

TABLE I

reducing agent	Fe ⁺³ reduced to	Ti ⁺⁴ reduced to	V ⁺⁵ reduced to	Cr ⁺⁶ reduced to	Mo ⁺⁶ reduced to
(1) an active metal (Zn, Al, Cd) + excess of acid	Fe ⁺²	Ti ⁺³	V ⁺³ V ⁺²	Cr ⁺³ Cr ⁺²	Mo ⁺³
(2) Zn Bi Pb	Fe ⁺² Fe ⁺² Fe ⁺²	Ti ⁺³ Ti ⁺³ (1) Ti ⁺³	V ⁺² V ⁺⁴ V ⁺²	Cr ⁺³ -- --	Mo ⁺³ (2) Mo ⁺⁵ or Mo ⁺³ Mo ⁺³
(3) Silver in HCl solution	Fe ⁺²	not red. in 1 NHCl sol.	V ⁺⁴ V ⁺³	Cr ⁺³	Mo ⁺⁵ (2)
(4) Stannous chloride in HCl solution	Fe ⁺²	Ti ⁺³ (partial)	V ⁺² V ⁺³ , V ⁺⁴	Cr ⁺³	Mo ⁺⁵ , Mo ⁺³ (2)
(5) Mercury in HCl solution	Fe ⁺²	not reduced	V ⁺⁴ (2)	Cr ⁺³	Mo ⁺⁵ (2)
(6) hydrogen sulfide	Fe ⁺²	not reduced	V ⁺⁴	Cr ⁺³	precipitated
(7) sulfur dioxide	Fe ⁺²	not reduced	V ⁺⁴	Cr ⁺³	partial

Chart adapted from Elementary Quantitative Analysis, Willard and Furman, third edition, page 203. D. Van Nostrand Company, 1941.

- (1) Complete at high acidity.
- (2) Reduction proceeds to a greater extent at higher acidities. At low acidities, reduction to V⁺⁴ or Mo⁺⁵ is quantitative.

Knecht and Hibbert¹ reported that in reducing mixtures of titanium and iron, especially when much iron was present, at least twenty minutes was required to complete the reduction process.

¹ Knecht, E. and E. Hibbert, New Redn. Methods in Vol. Analysis, page 13. Longmans, Green, and Company, 1918.

1. The first part of the paper discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study.

2. The second part of the paper presents the results of the study. It includes a detailed description of the data collected and the analysis performed. The results are presented in a clear and concise manner, with appropriate use of tables and figures to illustrate the findings.

3. The third part of the paper discusses the implications of the study and the conclusions drawn from the results. It also provides a brief summary of the key findings and the overall contribution of the study to the field.

4. The final part of the paper includes a list of references and a list of figures. The references are listed in alphabetical order, and the figures are numbered according to their position in the text.

A very old volumetric method for ferric iron is that of Mohr¹, in which iron is reduced by acidified potassium iodide, the liberated iodine being titrated with thiosulfate. Special precautions² have to be observed, however, for accurate results.

Somewhat similar methods are described by Heisig³, where potassium iodate is used in the volumetric determination of ferrous ion, and Lang⁴, where the iodometric determination of ferrous iron is based on the formation and determination of iodine cyanide.

Manchot has developed the bromometric method of analysis, and has applied it to many determinations. The iron procedure was worked out by Manchot and Oberhauser⁵. The basic principle in this type of analysis is the titration of free bromine by arsenious acid solutions. The principle, of course, may be applied to any reaction which will produce or consume bromine, if the reaction proceeds quantitatively and without unforeseen difficulties. The bromine solution may be one of the following: a water solution which is limited to 1/30 N because of instability; a solution in 20-22% of hydrochloric acid or in 1 N potassium bromide; or a glacial acetic acid solution in bromine. (The latter two solutions may be 0.1 N.) The stability of the solutions increases in the order

1 Mohr, Annalen, Volume 105, page 53. 1858.

2 Ferrey, Quart. J. Pharm., Volume 3, page 471. 1930.

3 J. Am. Chem. Soc., Volume 50, page 1678. 1928.

4 Zeut. Anorg. Allgem. Chem., Volume 142, page 229. 1925.

5 Z. Anal. Chem., Volume 67, page 196. 1926.

given. Many indicators have been suggested by other workers, but Manchot recommends an indigo carmine solution (0.2%). With colored solutions such as chromic and iron mixtures, the end point can be detected more easily with 0.2 gm. of indigo carmine and 0.2 gm. of styphnic acid (trinitro-resorcinol) dissolved in 100 ml. of water. It is best to add the indicator (a few drops) towards the end of the titration. Manchot and Oberhauser¹ have studied the equilibrium relationships in the titration of arsenious acid with bromine solution. They have found that if the concentration of hydrochloric acid is kept below 24%, a system will never arise in which the reaction is incomplete, regardless of the addition of potassium bromide in the various procedures. In the iron procedure², the iron is first reduced by sulfurous acid or electrolytic cadmium. The acid ferrous solution is then treated with about one gram of potassium fluoride and 20 cc. of approximately 15% hydrochloric or sulfuric acid solution. An excess of 0.1 N bromine solution in 1 N potassium bromide is added, and, after standing one or two minutes, the back titration is made with arsenious acid. Phosphoric acid may be substituted for the potassium fluoride, enough being added so that the solution contains 2-10% phosphoric acid. If the phosphoric acid concentration exceeds 15%, the indicator change is retarded.

In addition to the methods just mentioned, there are a few so-called direct methods for the analysis of iron. These employ stannous chloride,

1 Z. Anorg. Allgem. Chem., Volume 139, page 40. 1924.

2 Z. Anal. Chem., Volume 67, page 196. 1926.

The first thing I noticed when I stepped out of the car was the smell of fresh air. It was a relief after being stuck in traffic for hours. I walked towards the entrance of the park, feeling a sense of anticipation. The path was well-maintained and led me through a series of beautiful gardens. I saw many colorful flowers and plants that I had never seen before. The children were playing happily in the sandbox, and the old man was sitting on a bench, watching them. I felt a sense of peace and tranquility. The sun was shining brightly, and the birds were singing. It was a perfect day to be in the park. I took a deep breath and enjoyed the moment. The world was so beautiful, and I was so lucky to be here. I smiled and continued walking, feeling a sense of joy and happiness. The park was a wonderful place, and I was glad to have found it. I would come back here often, to enjoy the beauty of nature and the peace of the park. It was a special place, and I was lucky to have discovered it. I felt a sense of pride and accomplishment. I had found a place that was perfect for me. I was so happy, and I knew that this was my chance to live a better life. I was going to make the most of it, and I was going to enjoy every moment of it. The park was a wonderful place, and I was glad to have found it. I would come back here often, to enjoy the beauty of nature and the peace of the park. It was a special place, and I was lucky to have discovered it. I felt a sense of pride and accomplishment. I had found a place that was perfect for me. I was so happy, and I knew that this was my chance to live a better life. I was going to make the most of it, and I was going to enjoy every moment of it.

titanous¹ solution, or mercurous nitrate solution. In each case, ferric ion is titrated directly with one of the solutions. The chief disadvantage in the use of stannous and titanous solutions lies in the fact that they are unstable in air, and special precautions must be taken to protect the solution. Also, frequent re-standardizations are required.

The reactions between ferric ion and stannous and titanous ions are simple enough, and need no further explanation. Knecht and Hibbert's² specialized treatise on titanous solutions gives full details on the procedures. Some workers disagree on the amount of thiocyanate indicator necessary. Knecht and Hibbert claim that 5 ml. of ten per cent thiocyanate solution is needed, while Subbaraman and Krishnaswami³, whose work will be discussed later, claim that only a few drops of solution are needed for a sharp end point.

Bradbury and Edwards⁴ describe a direct method of titration, in which ferric ion is titrated with mercurous nitrate solution in the presence of an excess of ammonium thiocyanate. The method is shown to be accurate, both for direct determination of ferric ion and for total iron, following potassium permanganate determination of ferrous iron. Hydrochloric acid interferes with the reaction when present in concentrations of greater than 0.1 N, causing the titration values to be one to two per cent higher. The minimum quantity of thiocyanate required corresponds to ten equivalents of thiocyanate per equivalent of ferric ion. The mechanism of the reaction and the properties of the complex formed are not clear.

1 Knecht, E. and E. Hibbert, New Redn. Methods in Vol. Analysis, Longmans, Green and Co. 1918.

2 Knecht, E. and E. Hibbert, New Redn. Methods in Vol. Analysis, Longmans, Green and Co. 1925.

3 Proceedings of Indian Acad. of Sc., 11A, pages 106-115. 1940.

4 J. of Soc. of Chem. Ind., Transactions, Volume 59, pages 96-98. 1940.

The fact that zinc reduces titanium to titanous ions was until recently considered a serious drawback in the use of the Jones reductor in many mineral and ore analyses of iron. Since titanium usually is the only reducible metal which occurs with iron in appreciable quantities, in ordinary soil and rock analyses one will readily see that an easy method for eliminating or correcting the titanium effect would greatly increase the use of the metallic reductors which also reduce titanium. Gooch and Newton¹ suggested a procedure to eliminate titanous ions by adding bismuth oxide, cupric oxide, or cupric sulfate, which re-oxidizes the titanium selectively. After filtration from the excess of oxidizing agent and reduced product formed, the iron solution is titrated with permanganate solution. More recently, Thornton and Roseman² attained the same result by simply bubbling air through the solution for ten to thirty minutes. The latter procedure was shown to have little effect on the ferrous iron, but when appreciable quantities of titanium are present, considerable time is required for complete re-oxidation of the titanous ions. Troug and Pearson³ have improved the method of aeration by the following procedure:

If, after passage of the solution through a Jones reductor, a violet color cannot be seen after examination against a white background, one can assume that less than 0.1 mg. of titanium is present. This small amount will be quantitatively oxidized by stirring the solution vigorously

1 Am. J. Sci., Volume 23, page 365. 1907.

2 J. Am. Chem. Soc., Volume 57, pages 619-621. 1935.

3 Ind. and Eng. Chem., Anal. Ed., Volume 10, pages 631-632. 1938.



for three minutes in a 400-600 ml. beaker. If after reduction a violet color can be seen, then one can assume that 0.1 mg. or more titanium is present. This is quantitatively oxidized by adding 50 ml. of distilled water to the solution and stirring vigorously for at least three minutes after the last trace of violet has disappeared. The water which is added should be in equilibrium with air, so as to contain considerable dissolved oxygen. The total solution should be kept as small as possible (200-250 ml.). since stirring has been found more effective in a minimum total volume of solution. This method of determining iron gives very good results when **very** small quantities of titanium are present, and when the quantitative estimation of titanium is not desired.

Nicholson¹ describes a short volumetric method, based upon the aeration process of Troug and Pearson, for the determination of iron and titanium in silicates. The percentage of iron is determined after aeration, as previously described, and then a second titration is made without aeration. The difference represents interfering substances, such as titanium, chromium, molybdenum, vanadium, uranium, or columbium. All are extremely unstable, except V^{+4} , U^{+4} , and Fe^{+2} . Of all the interfering substances in the determination of iron after zinc reduction, titanium is ordinarily the only element present in appreciable quantities. Thus the difference is usually taken as representing the titanium content. During the course of this paper, an attempt will be made to present a new method by which accurate results for the amounts of both

¹ Bull. of Am. Ceramic Soc., pages 331-4. 1941.

titanium and iron can be obtained simultaneously in one titration without the aeration procedure.

A simple procedure for the volumetric estimation of iron and titanium in the presence of each other has been long lacking. Iron in the presence of large quantities of titanium is usually determined by a selective reduction process. Hydrogen sulfide is usually used in reducing the iron, leaving the titanium unaffected. Excess hydrogen sulfide is destroyed by boiling, and the titration of ferrous ions is made as usual with permanganate. The method has received extensive study by Wells and Mitchell, Coppadoro, Washington¹, McBride and Scherrer, Hillebrand², Lundell and Knowles³, and Subbaraman and Krishnaswami.⁴ All agree on the following points: good results are obtained only in acid solutions below about three per cent; pure hydrogen sulfide must be used; adequate time (one to three hours) must be allowed for the reduction of iron; and care must be taken to remove hydrogen sulfide by boiling after the completion of the reduction process. Some suggest sweeping out hydrogen sulfide with carbon dioxide gas, in addition to boiling. Subbaraman and Krishnaswami⁴ give an improvement in the volumetric estimation of iron and titanium, and its application is made in

1 The Chemical Analysis of Rocks, pages 163-165.

2 Analysis of Silicate and Carbonate Rocks, page 166. 1919.

3 J. Am. Chem. Soc., Volume 43, page 1563. 1921.

4 Proceedings of Indian Acad. of Sc., 11A, pages 106-115. 1940.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes that proper record-keeping is essential for transparency and accountability, particularly in financial matters. The text outlines various methods for organizing and storing data, suggesting that digital tools can be highly effective for this purpose. It also mentions the need for regular audits to ensure the integrity of the information.

2. The second section focuses on the role of communication in achieving organizational goals. It argues that clear and consistent communication is vital for ensuring that all team members are aligned and working towards the same objectives. The text provides examples of effective communication strategies, such as regular meetings and the use of collaborative platforms. It also highlights the importance of listening to feedback and being open to change.

3. The third part of the document addresses the challenges of managing resources efficiently. It notes that organizations often face constraints in terms of time, money, and personnel, and that finding ways to optimize these resources is a key to success. The text suggests several approaches, including prioritizing tasks, delegating responsibilities, and using technology to streamline processes. It also stresses the importance of monitoring progress and making adjustments as needed.

4. The final section discusses the importance of innovation and creativity in driving growth and development. It encourages organizations to foster a culture of innovation by encouraging employees to think outside the box and experiment with new ideas. The text mentions that innovation can lead to the development of new products, services, and business models, which can give a company a competitive edge in the market. It also notes that innovation is not just about technology but also about finding new ways to solve problems and improve efficiency.

5. In conclusion, the document emphasizes that success is achieved through a combination of effective record-keeping, clear communication, efficient resource management, and a commitment to innovation. It encourages organizations to embrace these principles and to continuously seek ways to improve their operations. The text ends with a call to action, urging readers to take the steps necessary to implement these strategies in their own organizations.

the analysis of ilmenite with good results. This is a case in which the aeration procedure fails because of the presence of large quantities of titanium. The procedure described uses the regular Jones reductor, in which a mixed solution of iron and titanium is reduced to ferrous and titanous ions, respectively. Treatment of the solution with standard permanganate solution would yield a titration value equal to the sum of titanium and iron present. Since titanous ions are easily oxidized in the air, the reduced solution was collected in a solution of ferric ions. The titanous ions then generated an equivalent of ferrous ions, and the whole was treated with permanganate. The titanium was determined by taking three or more samples of the solution. The first sample was used as a guide sample. It was reduced in the Jones reductor, and the titanous ions formed were immediately titrated with standard ferric solution, using four to five drops of thiocyanate indicator. (The use of 5 ml. of thiocyanate indicator, as suggested by several workers, was found unnecessary.) The volume of standard ferric solution used was low, because of air oxidation of titanium. To eliminate this error, the next sample was reduced as before and collected in a volume of standard ferric solution, 0.2-0.3 ml. less than that quantity needed. This volume was, of course, estimated from the previous titration value, which was expected to be low. The titration was then completed, using thiocyanate indicator as before. By using this modification consistently, accurate results were obtained. To illustrate the correction obtained by having a guide sample, in the first experiment, when 50 ml. of a mixed titanium and iron solution were reduced and collected in a flask

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with no previous addition of ferric solution, 23.45 ml. of standard ferric solution was used (0.09769 gm. titanium dioxide). In the second experiment, the 50 cc. mixture was reduced and collected in 23.25 ml. of standard ferric solution, and the solution was titrated to an end point with thiocyanate indicator. Also, a total of 23.55 cc. of ferric solution was used (0.09811 gm. titanium dioxide), which is very close to the true value, 0.09820 gm. titanium dioxide. The iron content was obtained by subtraction. In the following table of analyses of mixtures of iron and titanium solutions, taken from a weight burette, it is shown that the maximum error in any determination is about 0.4%.

TABLE II

ANALYSIS OF MIXTURES OF IRON AND TITANIUM

Quantities taken		Quantities found		Errors per cent	
Fe ₂ O ₃ g.	TiO ₂ g.	Fe ₂ O ₃ g.	TiO ₂ g.	Fe ₂ O ₃ g.	TiO ₂ g.
0.0714	0.1246	0.0712	0.1248	-0.27	+0.16
0.0840	0.1108	0.0842	0.1108	+0.25	-0.0
0.0914	0.1012	0.0916	0.1008	+0.22	-0.40
0.0972	0.0988	0.0970	0.0984	-0.21	-0.40
0.1002	0.0890	0.1002	0.0892	-0.0	+0.22
0.1014	0.0816	0.1010	0.0816	-0.37	-0.0
0.1102	0.0727	0.1104	0.0724	+0.19	-0.43

The analysis of ilmenite was made by taking 1-1.5 gm. of the finely crushed sample and fusing it in a hard glass test tube with 10-12 gms. of potassium acid sulfate until decomposition is complete. The fused mass is then digested with sulfuric acid (1:4) until extraction of soluble matter is complete. Silica which separates may be filtered off, ignited, and weighed, if required. Otherwise, no filtration is necessary, and the

The first part of the paper discusses the importance of understanding the underlying mechanisms of the observed phenomena. This is followed by a detailed description of the experimental setup and the data collection process. The results of the experiments are then presented, showing a clear correlation between the variables studied. Finally, the paper concludes with a summary of the findings and suggestions for further research.



The data presented in the graph clearly indicates a positive linear relationship between time and temperature. This suggests that the process being studied is exothermic and occurs at a constant rate. The experimental results are in good agreement with the theoretical predictions, confirming the validity of the model used.

entire acid extract may be transferred to a volumetric flask and diluted with water up to the mark. (Concentration of sulphuric acid in the solution can range from ten to fifteen per cent without detriment to ease of operation or accuracy of results.) Fifty cc. portions are withdrawn from the volumetric flask for estimation of titanium, and 100 ml. portions, for estimation of iron. The determinations are carried out as described for the above titanium and iron mixtures. It will be noticed that the determination of iron and titanium by the above procedure requires two separate titrations and two separate standard solutions. In this report, a method will be pointed out by which the above analysis can be made with a single titration with a single standard solution, resulting in greater accuracy.

The fact that titanium is the ninth most common element and widely distributed in nature makes its quantitative estimation important, especially in the analysis of rocks and ores. Its presence is usually in appreciable quantities so that it cannot be ignored. Many ways have been devised to eliminate or to determine titanium in ore and rock analyses, some of which have already been pointed out. Amalgamated zinc cannot be used for the reduction of iron, since titanium would also be reduced. Stannous chloride cannot be used if titanium is to be determined later in the same solution, or if a correction is to be made for vanadium, because the state of oxidation is unknown at the time of titration. The reduction must be made by hydrogen sulfide or sulphur dioxide, both of which reduce vanadium to the quadrivalent state, which is then oxidized by permanganate to the quinquivalent state, causing slightly high results for iron. Probably the best procedure is given by Walden, Hammett, and Edmonds.¹ The

¹ J. Am. Chem. Soc., Volume 56, page 350. 1934.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes the need for transparency and accountability in financial reporting.

2. The second part of the document outlines the various methods and techniques used to collect and analyze data. It includes a detailed description of the experimental procedures and the statistical analysis performed.

3. The third part of the document presents the results of the study. It includes a series of tables and graphs that illustrate the findings of the research. The data shows a clear trend of increasing activity over time.

4. The fourth part of the document discusses the implications of the findings. It suggests that the results have significant implications for the field of study and may lead to further research in this area.

5. The fifth part of the document provides a conclusion and summarizes the key points of the study. It reiterates the importance of accurate record-keeping and the need for ongoing research in this field.

6. The sixth part of the document includes a list of references to the sources used in the study. It provides a comprehensive overview of the literature on the topic.

7. The seventh part of the document contains a list of appendices. These include additional data, figures, and tables that are not included in the main body of the text.

8. The eighth part of the document is a list of footnotes. These provide additional information and clarification on the points made in the text.

9. The ninth part of the document is a list of acknowledgments. It thanks the individuals and organizations that provided support and assistance during the course of the study.

10. The tenth part of the document is a list of the authors. It provides the names and affiliations of the individuals who conducted the research and wrote the document.

iron is reduced by a silver reductor in hydrochloric acid solution. Titanium and chromium are not affected by the silver, and vanadium is reduced to the quadrivalent state. There is no error due to the vanadium, however, since the titration is made in a high acid medium with ceric sulfate or potassium dichromate solution, which does not affect V^{+4} . The determination of titanium must now be made by the colorimetric method in another solution, since cerium or chromic ions would interfere.

S. S. Cole and C. A. Kumins¹ describe procedures for the determination of iron, vanadium, and titanium in the presence of one another. The percent of titanium has to be obtained with that of vanadium, or in conjunction with iron and vanadium. Thus the accuracy of the titanium determination depends upon the errors involved in the iron and vanadium analysis. Iron was determined by the method just described, using a silver reductor and cerium solution. Vanadium was determined in the second titration with another portion of solution by adding 50 ml. of 10 M sulphuric acid and bringing to sulphur trioxide fumes to drive off hydrochloric acid. This is followed by diluting to 200 ml. and cooling to 20° C. One drop of orthophenanthroline indicator was added, and the solution was adjusted with 0.1 N cerium sulfate or 0.1 N ferrous sulphate to obtain tetravalent vanadium. The mechanism of the valence adjustment may be expressed thus:



When the indicator turns red, both Fe^{+2} and V^{+4} are present, but no V^{+5} can be present. The addition of cerium sulphate oxidizes Fe^{+2} to Fe^{+3} , and the indicator turns greenish blue. Now Fe^{+3} , V^{+4} , and V^{+5} may be present. The addition of ferrous sulphate reduces V^{+5} to V^{+4} and is

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complete when the indicator turns red, showing a trace of Fe^{+2} . The solution was boiled to destroy the indicator, and was immediately titrated with 0.1 N potassium permanganate.

In a third titration, a third portion of solution was reduced in a zinc reductor, forming Ti^{+3} , V^{+2} , Fe^{+2} . The usual titration with ferric solution gave erratic results, probably because of the slow oxidation of vanadium, or because of incomplete reduction of titanium in the presence of vanadium. This was finally overcome by using lightly amalgamated zinc and titrating the reduced solution above 90°C . The titer must be corrected for vanadium previously determined. The reduced solution could be titrated with 0.1 N potassium permanganate until the appearance of an end point, after which the solution was heated to boiling, and titration continued to a permanent end point. At 90°C . or higher, it was found that the oxidation of vanadium went to completion rapidly. The permanganate titer was corrected for iron and vanadium to obtain titanium.

M. Axt and M. Le Roy¹ have developed an aeration method similar to that of Thornton and Roseman previously mentioned. Instead of freshly aerated water, air was bubbled through the solution. A cold 5% sulphuric acid solution of iron is stable. It was found that solutions containing 0.045-0.116 gm. were oxidized quantitatively in 3-8 minutes.

In the analysis of the mixture of ferric ion and titanous ion, Isibasi and Kadoya² reduced the mixture with a suitable amalgam such as zinc, and

¹ Axt, M. and M. Le Roy, L'ingénieur chimiste, Volume 24, pages 28-31. 1940.

² J. Chem. Soc. of Japan, Volume 62, pages 316-318. 1941.

1. The first part of the document is a letter from the President of the United States to the Congress, dated January 3, 1801. It is a very important document, as it contains the President's first annual message to Congress. The letter is written in a formal, dignified style, and it is one of the most important documents in the history of the United States.

2. The second part of the document is a report from the Secretary of the Navy, dated January 10, 1801. It is a very important document, as it contains the Secretary's report on the state of the Navy. The report is written in a formal, dignified style, and it is one of the most important documents in the history of the United States.

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6. The sixth part of the document is a report from the Secretary of the State, dated January 10, 1801. It is a very important document, as it contains the Secretary's report on the state of the State. The report is written in a formal, dignified style, and it is one of the most important documents in the history of the United States.

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titrated with potassium permanganate to determine the sum of the two metals present. In a second titration, a portion of the reduced mixture was titrated with the original Ti^{4+} and Fe^{3+} mixture. Then the oxidation of titanous ion by the ferric ion takes place, forming an equivalent of ferrous ion, and the ratio of iron to titanium was determined. Similar procedures were used with mixtures of iron and uranium, iron and vanadium, and titanium and vanadium. This procedure is rather awkward, and requires two titrations. Some error would probably be introduced in titrating with the reduced solution, because of the air oxidation of the titanous ions.

Novakovskii and Isionskaya¹ have suggested a rapid method for the determination of titanium in the presence of iron. They used a few drops of 0.5% solution of indigo carmine, and titrated with potassium dichromate or ferric chloride. The method is reported to be very accurate and rapid, and is recommended for plant analysis of ferrotitanium. The titration of titanium in air will give low results, due to the air oxidation of the titanous ions, and low results would be expected in the above procedure. The work of the above authors was not reviewed until this research was completed. It was found that indigo carmine was a very accurate indicator for the titanium end point. There is one difficulty in the use of potassium dichromate. The green coloration of the chromic ions sometimes obscures the blue end point of indigo carmine, especially if large amounts of titanium are present. A better visual end point may be obtained by using indigo tetrasulfonate, which turns red instead of blue. The difference in oxidation reduction potential between the two indicators is slight, compared to the potential break obtained.

¹ Zavodskaya Laboratoriya, Volume 9, Number 1, pages 103-104. 1940.

D. I. Ryabchikov and V. G. Sil'nichenko¹ have developed a procedure for the determination of iron by potentiometric titration. They reduced with a solution of cuprous chloride (about 0.1 g.) in two to three ml. of a saturated salt solution, and acidified slightly with hydrochloric acid. They claimed that the titration with potassium permanganate would be accompanied by the oxidation of the excess reducing agent and the oxidation of the reduced iron. The first break in the titration curve will be at 300-400 mv.; the second break is at 650-800 mv. (These values apply only to samples high in iron. The potentials will be considerably lower at low iron content.)

In a new procedure for the determination of iron, a titanium hydride product was used in place of stannous chloride as a reductor, and indigo sulfonates were used for the titanium end point. Permanganate, cerium, and dichromate solutions were used with the orthophenthroline ferrous complex and sodium diphenylamine sulfonate as indicators for the latter two solutions, respectively. Numerous potentiometric titrations were made to check the indigo sulfonate end points. The latter end points were found to be very sharp and accurate, with no interference in the following iron end point. Results for the iron determinations agreed very well with the true values. The time required for the determinations was very short.

¹ J. Applied Chem. (U. S. S. R.), Volume 12. 1907-1911. In French, 1911, 1939.

The first part of the paper discusses the importance of maintaining accurate records of all transactions. It is essential for the business to have a clear and concise record of all income and expenses. This will allow the business to track its financial performance over time and identify areas for improvement. The second part of the paper discusses the importance of maintaining accurate records of all assets and liabilities. This will allow the business to track its net worth over time and identify areas for improvement. The third part of the paper discusses the importance of maintaining accurate records of all taxes paid. This will allow the business to track its tax liability over time and identify areas for improvement. The fourth part of the paper discusses the importance of maintaining accurate records of all debts. This will allow the business to track its debt liability over time and identify areas for improvement. The fifth part of the paper discusses the importance of maintaining accurate records of all equity. This will allow the business to track its equity over time and identify areas for improvement. The sixth part of the paper discusses the importance of maintaining accurate records of all other financial information. This will allow the business to track its overall financial performance over time and identify areas for improvement.

By maintaining accurate records of all financial information, the business can ensure that it is always up-to-date on its financial performance and can make informed decisions about its future.

CHAPTER II

DISCUSSION OF THE TITANIUM HYDRIDE PRODUCT

The method for the preparation of titanium hydride has been patented¹ by Peter P. Alexander. Titanium oxide is very refractory and has an extremely high heat of formation. Metallic titanium, as reduced by the usual methods, is treated similarly to boron and silicon. In the electrolysis of calcium chloride in the presence of titanium oxide, the calcium set free effects the liberation of the titanium. The metal is also prepared by reducing titanium chloride or double chloride with sodium. The metal should not be kept in open air, because the amount of oxygen in the air is sufficient for the titanium to ignite at fairly low temperatures. Once the metal is ignited, it burns almost instantaneously with a dazzling white heat, forming titanium dioxide. Alexander found that, although ordinary molecular hydrogen did not have an appreciable effect, even at high temperatures, on certain refractory oxides, as chromic oxide and titanium dioxide, a stream of hydrogen generated from a metallic hydride readily reduced the oxide, when heated to the proper temperature in a partial vacuum. The hydrogen gas was in a very pure and active form (nascent hydrogen) when generated from the hydride. There are many metals which occlude large volumes of hydrogen at relatively high temperatures and normal atmospheric pressure, and they will evolve the occluded gas in a vacuum at a somewhat higher temperature. Using the apparatus shown in Figure 1, some of the most refractory oxides can be readily reduced by simply regulating the partial vacuum and temperature.

¹ Patent No. 2,038,402, April 21, 1936.

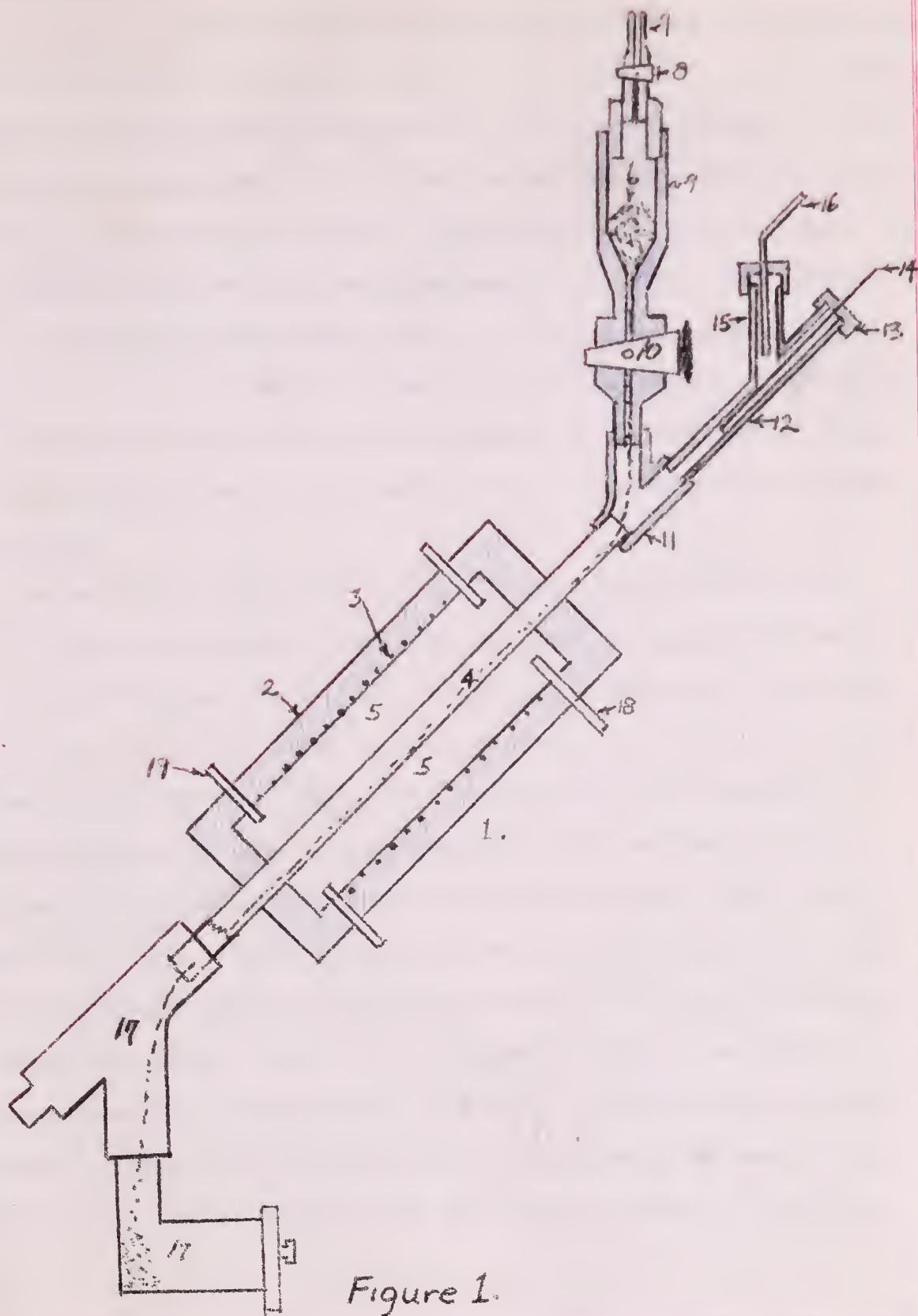


Figure 1.

In Figure 1, number (1) represents an electric furnace which is mounted at an angle with the horizontal. The furnace is made up of a hollow tubular member (2) provided with a heating coil (3) connected to a suitable source of electrical energy (not shown). A tubular refractory member (4), which is porous and made of aluminum oxide or alundum, extends through the member (2) and slightly beyond the upper and lower ends of the latter. The portions of the tube (4) which extend beyond member (2) are glazed to prevent the admission of air to the tube. The space within (2) and around the outside of tube (4) may be filled with a suitable metal or metallic hydride (5), such as calcium hydride, or any other metal capable of occluding large volumes of hydrogen.

The metal or metallic hydride should be in a finely divided state. At the upper end of tube (4) a means is provided for supplying a measured quantity of refractory oxide (6) to the tube (4). In order to supply the oxide, a pipe (7) is connected to a source of the oxide supply. The lower end of the pipe (7) is provided with a stopcock (8), which may admit a measured quantity of oxide into the receptacle (9). Receptacle (9) is provided with a stopcock (10) for admitting the refractory oxide to (4) by means of a T (11), carrying at its outer end a suitable tube (12), which extends in the same axial direction as the tube (4), and which is actually a continuation of (4). Tube (12) is provided at its upper end with a closure member (13), through which a rod (14), preferably made of tungsten or other suitable material, is mounted for reciprocating movement within tube (4). Rod (14) is used to clean tube (4) and to push the refractory

oxide through the tube. Tube (12) is also provided with an extension (15), which carries a pipe (16) connected to a vacuum pump which is not shown. The lower end of the tube (4) is closed by a receptacle (17), into which the pure metal reduced within the tube (4) may be collected.

In operation, the stopcock (10) is closed, and receptacle (9) is filled with the refractory oxide to be reduced. The member (2) is filled with a finely divided hydride or a metal (5) capable of occluding large quantities of hydrogen. In the case of titanium dioxide, calcium could be used. If a metal such as calcium is used, it is heated to a dull red heat by means of the heating coil (3), while hydrogen is supplied to the finely divided metal through an inlet pipe (18). The hydrogen flows out of the receptacle (2) through an outlet pipe (19). At dull red heat, calcium absorbs a very large quantity of hydrogen, to form calcium hydride. This reaction is exothermic, and therefore consumes no energy. At this point, the hydrogen is shut off and the temperature is increased. At about 675° C., evolution of hydrogen from the calcium hydride will begin in a partial vacuum. The temperature of the furnace is now increased to 1000° C. or higher, while a vacuum of about 100 microns is established. Stopcock (8) is now closed, and (10) is opened to admit a desired quantity of refractory oxide to tube (4). The oxide gradually moved downward in the tube (4), due to the inclination, and is subjected to the action of the nascent hydrogen. The latter comes out of the hydride at a great speed, and is in a very pure and active condition. First it penetrates the porous tube (4), and quickly effects the reduction of the refractory oxide, leaving the reduced metal, which gradually moves into receptacle (17).

The complete reduction of chromic oxide may be effected in about six minutes. The rate of reduction depends upon the vacuum and temperature employed. Thirty thousand microns vacuum can be used, and the reduction still takes place quickly. The equations for the reactions with chromic oxide and titanium dioxide are as follows:



The water vapor produced is rapidly removed by the vacuum pump, and does not affect the evolution of hydrogen. The same calcium may be used over and over again by simply supplying the necessary quantities of hydrogen and re-heating. Calcium absorbs 850 volumes of hydrogen at dull red heat, and evolves the hydrogen in the nascent condition at 675°C . in a partial vacuum. Tantalum could be used for very refractive oxides, since it absorbs 740 volumes of hydrogen at a red heat, and readily evolves it at about 950°C . in vacuum. The choice of metal or hydride depends upon the oxide's being reduced, the temperature at which the hydrogen is readily evolved, and the amount of hydrogen absorbed. Other suitable metals, in addition to calcium and tantalum just mentioned, are palladium, chromium, and cobalt.

Since titanium readily forms the oxide in air at relatively low temperatures, with an almost instantaneous evolution of great quantities of heat, the metal can be prepared only by cooling in a vacuum (after reduction by hydrogen). If the titanium is cooled in an atmosphere of hydrogen, however, the product is not metallic titanium, but titanium hydride. Titanium hydride is a brittle solid, very stable at room temperature. It is not hygroscopic, and is fairly resistant to the attack of

dilute acids. When heated in air to about $350^{\circ}\text{C}.$, it decomposes slowly with the evolution of hydrogen gas. Figure 2 shows the effect of heat on various hydrides, as reported by Zeiverts¹. When the temperature is raised to the ignition of the hydrogen, the latter burns quietly, and completely surrounds the decomposing hydride. As soon as the hydrogen is all evolved from the hydride, however, the remaining titanium then ignites and burns in a fraction of a second with a dazzling white heat. When the titanium hydride is heated in a closed quartz vessel filled with hydrogen at normal pressure, the decomposition begins at about $350^{\circ}\text{C}.$, and reaches a maximum at about $800^{\circ}\text{C}.$ The remaining titanium powder sinters together at $1000^{\circ}\text{C}.$, producing an ingot of silver white metal, which is very hard and easily scratches glass.

Every gram of titanium hydride, when heated gradually to $900^{\circ}\text{C}.$, evolves 360 cc. of hydrogen. The remaining titanium still contains a little hydrogen in an occluded form, and can be removed at higher temperatures in vacuum. The total volume of hydrogen extracted from a gram of hydride, when it was heated to $1100^{\circ}\text{C}.$ in vacuum, was 398 cc.

$$(0.398) (47.90) = 19.064 \text{ liters of hydrogen/gm. atom Ti}$$

$$\frac{19.1}{11.2} = 1.70 \text{ gm. atoms of hydrogen/gm. atom Ti}$$

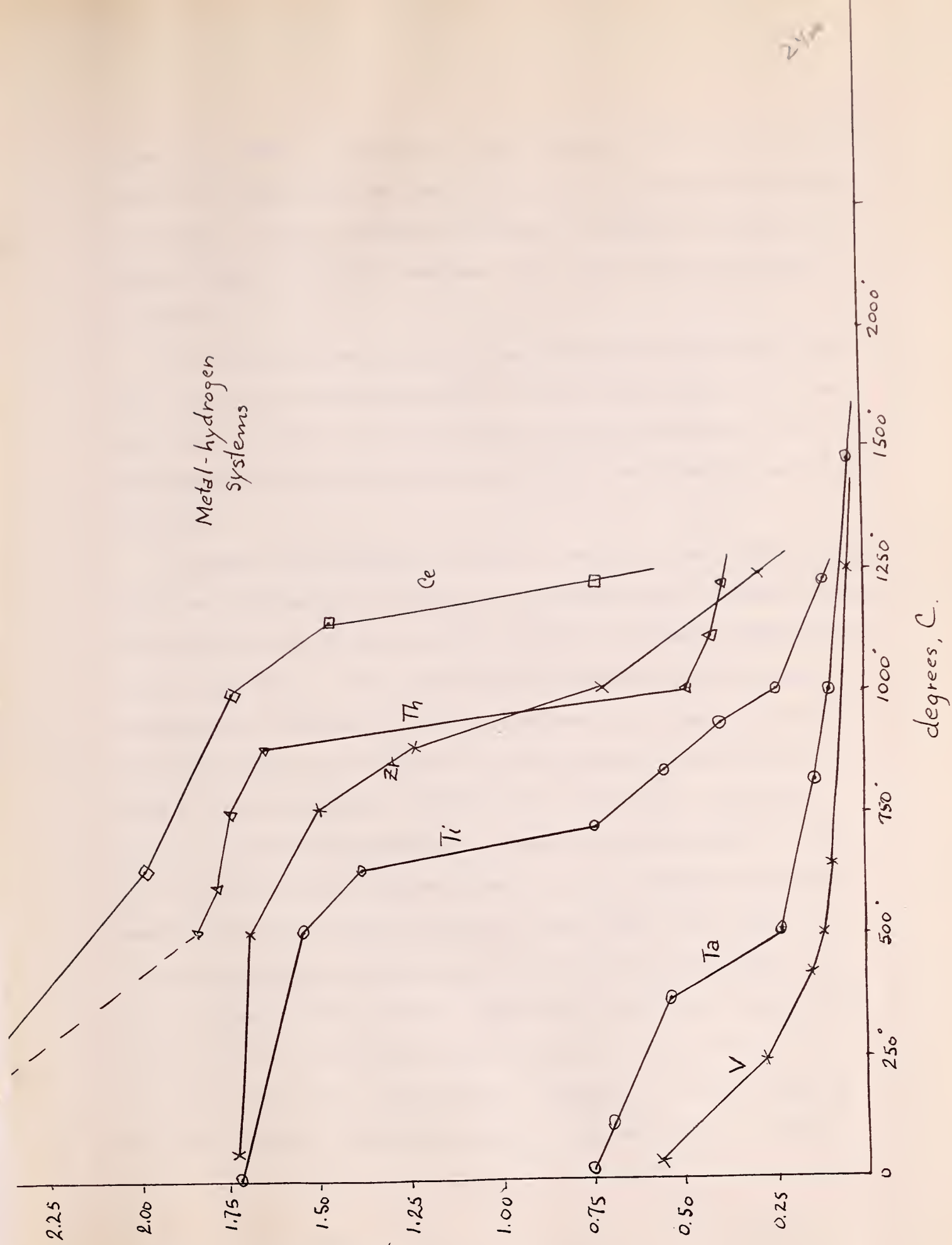
The investigations of Zieverts² and his co-workers have given strong evidence toward the conclusion that the black metallic products obtained when such metals as titanium, zirconium, thorium, vanadium, columbium, and

1 Z. Anorg. Chem., pages 141-153. 1923-1926. Summary, Z. Angew. Chem., Volume 21, page 37. 1929.

2 Z. Angew. Chem., Volume 21, page 37. 1929.

Gram atoms of hydrogen / Gram atom of metal

Metal-hydrogen
Systems



tantalum are heated in hydrogen are solid solutions. The quantity of hydrogen, and the temperature and pressure relations can be compared with those of palladium. Generally besides palladium, the elements occurring from three to five places after a rare gas in the long periods give hydrides of this sort.

The reducing actions of the titanium hydride and titanium metal were compared by taking weighed quantities of each for the reduction of known quantities of ferric iron. The solution of iron was tested with a drop of permanganate to be sure that no ferrous ion was present before starting the reduction.

In making this comparison, a number of assumptions were made as to the reduction accomplished by titanium in the valence states from zero to three. The assumptions are the same, however, for both the titanium metal and the hydride reductions. It was assumed that no reduction of the iron was accomplished by titanium in going from the metal to valence of plus two. Although I believe this assumption has some grounds, it does make the results of the following table indefinite and speculative. If titanium metal or titanium hydride powder is placed in an acid solution of ferric ions, the reducing action is very slow, if at all. It seems, therefore, reasonable to assume that in going from valence state zero to two, titanium loses electrons, and hydrogen ion forms hydrogen gas, while iron is not affected. (That is to say, the titanium must be in solution before it can react at an appreciable rate with iron.) Titanous ions are also very easily destroyed in the presence of hydrogen ion, and one would expect some competition between hydrogen ions and ferric ions in oxidizing

titanium from valence two to three, especially since the concentration of hydrogen ion greatly exceeds that of ferric ion. In going from valence state three to four, however, titanium is not affected nearly so much by acids, but very rapidly by ferric ions.

One would expect to get similar results in the following tables, since the same assumption is involved in both. This is not the case, however, since the table using titanium hydride shows that a great deal of reduction was accomplished by hydrogen, while on the same basis, the table using titanium metal shows no reduction by hydrogen. The only instance in which no reduction by hydrogen was shown in using the hydride occurred when the hydride was added to the hot acid solution, expelling hydrogen gas very rapidly. In using the titanium metal, in all cases the reduction was carried out slowly. It is very interesting to note that under the same conditions, the hydride was so much more effective.

TABLE III

POWDERED TITANIUM METAL AS A REDUCING AGENT

m.e. of Fe reduced	wt. of Ti metal, mgs.	m.e. Ti	m.e. Fe		
			m.e. Ti	red. by titrated Ti	m.e. iron reduced by H_2
3.38	98.0	4.10	0.66	1.99	----
3.78	122.0	5.02	1.27	2.50	0.04
3.49	128.7	5.38	1.72	2.52	----
3.19	113.0	4.72	0.91	1.74	----
2.76	93.5	3.90	0.73	1.54	----
3.52	137.2	5.72	1.90	2.56	----
4.10	183.0	7.64	3.00	3.28	----

TABLE IV

TITANIUM HYDRIDE AS REDUCING AGENT

m.e. Fe red	wt. of hydride mgs.	wt. of H ₂ in hydr. mgs.	wt. of Ti in hydr. mgs.	m.e. of Ti	m.e. titr.	m.e. iron red. by hydrogen	% iron red. by hydrogen	rate of heating and other cond- itions of re- duction
3.91	146.7	5.30	141.4	5.90	1.11	----	----	hydride was add-
4.83	218.6	7.85	210.7	8.82	3.02	----	----	ed to the hot
4.78	150.0	5.40	144.6	6.04	0.46	----	----	solution
2.59	142.4	5.10	137.3	5.72	2.22	----	----	hydride was added
2.85	153.5	5.50	148.0	6.18	2.54	----	----	to the hot soln.
2.93	122.5	4.40	118.1	4.92	0.81	----	----	hydride was added
3.11	130.5	4.70	125.8	5.24	1.32	----	----	to the hot soln.
3.30	88.6	3.20	85.4	3.56	1.12	0.86	25.8	rapid
2.75	90.6	3.30	87.3	3.64	1.39	0.50	18.2	rapid
3.16	112.9	4.00	108.9	4.50	1.79	0.45	14.3	rapid
3.95	117.6	4.20	113.4	4.74	1.89	1.10	28.0	moderate
3.30	86.6	3.10	83.5	3.48	1.30	1.12	33.9	moderate
3.95	103.2	3.70	99.5	4.15	1.51	1.31	33.2	moderate
2.94	90.7	3.30	87.4	3.65	1.36	0.65	22.5	moderate
3.17	63.0	2.30	60.7	2.54	0.40	1.03	32.2	moderate
6.70	195.9	7.05	188.8	7.88	3.11	1.93	28.8	moderate
5.39	174.2	6.30	167.9	7.00	2.94	1.33	24.6	moderate
4.87	99.2	3.55	95.6	3.98	0.81	1.70	34.9	slow
3.52	84.3	3.30	81.0	3.38	1.31	1.45	41.2	slow
4.00	83.0	3.00	80.0	3.34	1.45	2.11	52.7	slow
3.78	85.5	3.10	82.4	3.42	1.36	1.72	45.5	slow
3.70	91.0	3.30	87.7	3.66	1.42	1.46	39.5	slow
3.60	94.3	3.40	90.9	3.80	1.56	1.36	37.8	slow
4.00	100.0	3.60	96.4	4.03	1.61	1.58	39.69	slow

CHAPTER III

DISCUSSION OF THE INDICATORS

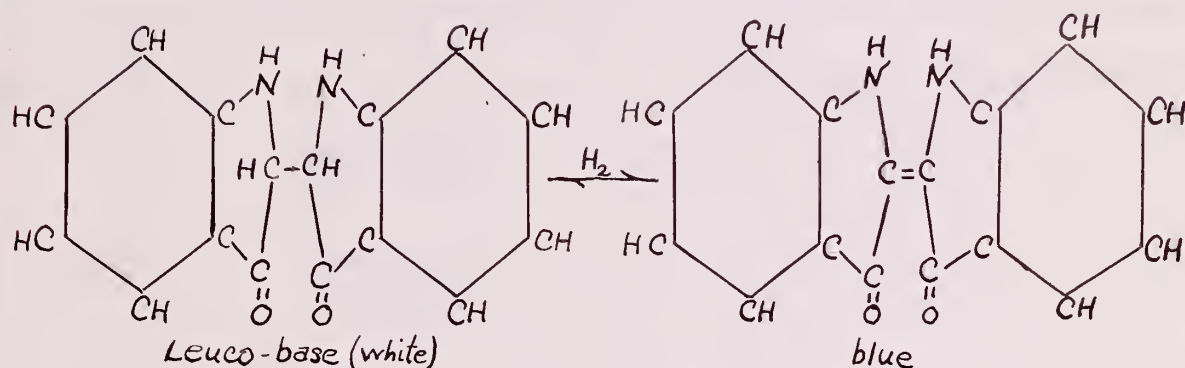
In order to eliminate the use of a potentiometric apparatus in determining the end point of the titanium and iron systems, a suitable indicator was found. The indicator, to be successful in this particular determination, had to meet the following requirements:

1. The oxidation-reduction potential at which the color change took place had to be rather low.
2. The color change had to be sharp and rapid.
3. The end point color had to be reasonably permanent (i. e., about two minutes).
4. The indicator had to be resistant to the action of strong mineral acids.
5. The indicator must not react with the common ions to form complexes or a new compound.
6. Reversability was desirable, but not essential.
7. The indicator solutions should be stable, easily prepared, and obtainable.
8. Only small quantities of indicator should be used, in order to make the blank very small or negligible.
9. The color change had to be such that it did not interfere with the next indicator for the iron end point, or an easy method for its destruction was necessary.

The di-, tri-, and tetrasulfonates of indigo meet the above nine conditions. The monosulfonate is rather insoluble in dilute acid solutions. In the first requirement, no mention is made of the exact oxidation-reduction potential that is required for the indicator to change color.

It is theoretically possible to calculate the range of the oxidation-reduction potential at the equivalence point, in which the indicator must also be located in order to be suitable. In selecting an indicator, however, one must consider the effects of the hydrogen ion concentration, the con-

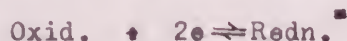
centrations of other ions in the solution, and the temperature. Usually, the latter two effects are small, compared with the hydrogen ion effect. The indigo sulfonates may be considered as acceptors (bases) of protons in the oxidized form, and donors (acids) in the reduced form. Therefore, the oxidation-reduction potentials are rather complicated functions of the pH and the ionic strength of the medium. Variations due to temperature changes are, fortunately, slight, and if the potential break between two systems is great, the above effects need to be considered only as rough estimates. The mechanism of the indigo color change may be represented thus (Baeyer, 1883):



The above picture does not represent all of the physical properties and certain reactions of indigo. It is generally agreed, however, that indigo-white in the isolated condition has two more hydrogens than indigo. Titration experiments were made by Clark¹ in which the oxidant was reduced, or the reductant was oxidized, at approximately constant pH. This furnished the value of \underline{N} , the number of electrons concerned in the process.

¹ Studies on Oxidation-Reduction, United States Public Health Department, Reprint No. 848, page 1669-1718. 1923.

It is reasonable to assume that the two electrons involved create two points which are potentially anionic, which then become seats of hydrogenation in the isolated compound. If this is so, the system may be represented thus:



In illustrating the effect the hydrogen ion concentration produces in the oxidation-reduction potential, we will assume that the oxidation product has neither acid nor basic properties. Thus, a shift in the hydrogen ion concentration will not alter the concentration of the oxidant. Then if we consider the reduction product as having taken on the properties of an anion in acquiring two electrons, we know nothing about the concentration of the anion red.[•]. To measure the concentration of the total reduction product, we must resort to equilibrium equations. These will take the following form¹

$$\frac{[\text{H}^+][\text{H Red}^-]}{[\text{H}_2 \text{ Red}^-]} = K_1 \quad (1)$$

$$\frac{[\text{H}^+][\text{Red}^{\bullet}]}{[\text{H Red}^-]} = K_2 \quad (2)$$

$$\text{Redn}_T = [\text{Red}^{\bullet}] + [\text{H Red}^-] + [\text{H}_2 \text{ Red}^-] \quad (3)$$

where redn_T = The total reduction product. (Active conc.)²

$$\left. \begin{array}{l} [\text{redn}^{\bullet}] \\ [\text{H Redn}^-] \\ [\text{H}_2 \text{ Redn}^-] \end{array} \right\} = \text{The active concentrations of the three possible forms in which the redn. product would exist.}$$

The oxid.-redn. reaction has been described by the equation--



- 1 This development is similar to that of William Clark, The Determination of Hydrogen Ions, 3rd edition, Williams and Wilkins Co. 1928.
- 2 It has been assumed for simplicity that activity and concentration are identical.

given by--

$$E_h = E - \left[\frac{RT}{2F} \right] \ln \left[\frac{\text{Redn.}}{\text{Oxid.}} \right] \quad (4)$$

(E_h = potential referred to hydrogen electrode)

Since the concentration of the oxidant is not affected by hydrogen ions and oxid. is equal to the total concentration of the oxidant, we have only to find an expression for redn.⁺ in terms of the total reductant concentration. This can be done with equations (1), (2), and (3) by substitution of (1) and (2) in (3) and solving for red⁺ as follows:

$$\begin{aligned} \text{Redn}_T &= [\text{Redn}^+] + \frac{[\text{Redn}^+][\text{H}^+]}{K_2} + \frac{[\text{H Redn}^+][\text{H}^+]}{K_1} \\ \text{Redn}_T &= [\text{Redn}^+] + \frac{[\text{redn}^+][\text{H}^+]}{K_2} + \frac{[\text{Redn}^+][\text{H}^+]^2}{K_1 K_2} \\ \text{Redn}_T &= [\text{Redn}^+] \left| 1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right| = [\text{Redn}^+] \left| \frac{K_1 K_2 + K_1 [\text{H}^+] + [\text{H}^+]^2}{K_1 K_2} \right| \quad (5) \\ \text{Redn}^+ &= [\text{Redn}_T] \left| \frac{K_1 K_2}{K_1 K_2 + [\text{H}^+] K_1 + [\text{H}^+]^2} \right| \end{aligned}$$

Now by substitution of (5) into (4) we have---

$$E_h = E - \left[\frac{RT}{2F} \right] \ln \left[\left[\frac{\text{Redn}_T}{\text{Oxid}} \right] \cdot \left[\frac{K_1 K_2}{K_1 K_2 + [\text{H}^+] K_1 + [\text{H}^+]^2} \right] \right] \quad (6)$$

Rewriting (6)-- and collecting constants--

$$E_h = E_0 - \left[\frac{RT}{2F} \right] \ln \left[\frac{\text{Redn}_T}{\text{Oxid}} \right] + \left[\frac{RT}{2F} \right] \ln \left| K_1 K_2 + [\text{H}^+] K_1 + [\text{H}^+]^2 \right| \quad (7)$$

(where $E_0 = E - \log K_1 K_2$)

$$f(x) = \frac{1}{x^2} = x^{-2}$$

Derivative of $f(x) = x^{-2}$ is $f'(x) = -2x^{-3}$

which can be written as $f'(x) = -\frac{2}{x^3}$

or $f'(x) = -\frac{2}{x^3}$ for $x \neq 0$

Therefore, the derivative of $f(x) = \frac{1}{x^2}$ is $-\frac{2}{x^3}$

for all $x \neq 0$. The function $f(x) = \frac{1}{x^2}$ is not differentiable at $x = 0$.

Example 2: Find the derivative of $f(x) = x^3$.

Solution: Let $f(x) = x^3$. Then

$$f'(x) = \frac{d}{dx} x^3 = 3x^2$$

Therefore, the derivative of $f(x) = x^3$ is $3x^2$.

Example 3: Find the derivative of $f(x) = \sqrt{x}$.

Solution: Let $f(x) = \sqrt{x}$. Then

$$f'(x) = \frac{d}{dx} \sqrt{x} = \frac{1}{2\sqrt{x}}$$

Therefore, the derivative of $f(x) = \sqrt{x}$ is $\frac{1}{2\sqrt{x}}$.

Example 4: Find the derivative of $f(x) = \ln x$.

Solution: Let $f(x) = \ln x$. Then

If the hydrogen ion concentration is kept constant, the last term in equation (7) is constant, and we have---

$$E_h = E - \left[\frac{RT}{2F} \right] \ln \left[\frac{\text{Redn}_T}{\text{Oxid}_T} \right] \quad (8)$$

In order to study the last term in (7), $\left[\frac{\text{Redn}_T}{\text{Oxid}_T} \right]$ is set equal to one.

Then we have---

$$E_h = E_o + \left[\frac{RT}{2F} \right] \ln \left[K_1 K_2 + [H^+] K_1 + [H^+]^2 \right] \quad (9)$$

TABLE V¹

Sulfonate of indigo	K ₁	K ₂
Leuco-indigo monosulfonate	1.6 x 10	less than 10
Leuco-indigo disulfonate	4.9 x 10	less than 10
Leuco-indigo trisulfonate	7.7 x 10	less than 10
Leuco-indigo tetrasulfonate	11.2 x 10	less than 10

In equation (9) and from TABLE V, one can easily see that the quantity, K₁K₂, is going to be very small, so that we may write--

$$E_h = E_o + \left[\frac{RT}{2F} \right] \ln K_1 [H^+] + [H^+]^2 \quad (10)$$

(In the calculations in this report, the quantity, K₁[H⁺], may also be neglected.)

Preparations of the indigo sulfonates have been given in detail by Bloxam (1906). M. X. Sullivan, B. Cohen, W. M. Clark² give detailed pro-

¹ This table was adapted from Studies on Oxidation-Reduction, United States Public Health Department, reprint No. 848. 1923.

² Studies on Oxidation-Reduction, United States Public Health Department, reprint No. 848, pages 1669-1718. 1923.

1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation

$$f(x) = \int_0^x \frac{1}{1+t^2} dt$$

It is shown that the function $f(x)$ is increasing and concave down on the interval $(-\infty, \infty)$.

2. In the second part of the paper, we consider the function $g(x)$ defined by the equation

$$g(x) = \int_0^x \frac{t}{1+t^2} dt$$

It is shown that the function $g(x)$ is an odd function and that it is increasing on the interval $(-\infty, \infty)$.

$$g(x) = \frac{1}{2} \ln(1+x^2)$$

3. In the third part of the paper, we consider the function $h(x)$ defined by the equation

$$h(x) = \int_0^x \frac{t^2}{1+t^2} dt$$

It is shown that the function $h(x)$ is an even function and that it is increasing on the interval $(-\infty, \infty)$.

4. In the fourth part of the paper, we consider the function $k(x)$ defined by the equation

$$k(x) = \int_0^x \frac{t^3}{1+t^2} dt$$

It is shown that the function $k(x)$ is an odd function and that it is increasing on the interval $(-\infty, \infty)$.

cedures which have been tested by analysis for the preparation of indigo sulfonates. The sulfonates are formed by the action of sulphuric acid, and are dependent upon the time, temperature, and strength of sulphuric acid. Room temperature and ten to twenty parts of ordinary concentrated sulphuric acid to one of indigo are conditions yielding the monosulfonic acid. Warming, using the same conditions as for the monosulfonate, yields the disulfonic acid, indigo carmine. Moderate warming with sulfuric containing 15% excess sulphur trioxide gives the tri-sulfonic acid, while the tetrasulfonic acid is obtained by using high temperatures and fuming sulfuric acid containing 20% excess sulphur trioxide. As the degree of sulfonation increases, the insoluble indigo is converted into products of higher solubility. Consequently, in the crystallization of the salts, the tendency is for the contaminate to be one or more of the lower sulfonates. The aim is to carry the reaction as completely as possible to the stage desired without oversulfonation.

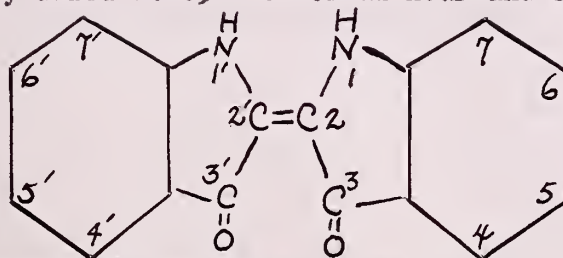
There are a number of ways in which to prepare and store the indigo indicators. For the work reported in this paper, indigo disulfonate and indigo tetrasulfonate were used. Their preparation was made as follows:

For the disulfonate, 10 gms. of resublimed indigotin, 16.5 ml. concentrated sulphuric acid, and 15.0 ml. of fuming sulphuric acid were mixed in an Erlenmeyer flask. The flask was kept just under 50° C. for about three hours; then the whole was cooled in ice and diluted with 20 ml. of distilled water to make about 50 ml. of indicator solution. This solution was filtered through a sintered glass crucible before using and diluted to a one per cent solution with respect to indigotin.

The color of the solution is a deep blue, and the end point with titanium goes from a very light greenish-yellow color in titanous solution to a deep blue at the titanous end point. Less than one drop of 0.1 N potassium dichromate, ceric sulfate, or potassium permanganate was needed to obtain a sharp color change. Heating had little effect.

Indigo tetrasulfonate was prepared by taking ten grams of resublimed indigotin and adding 40 ml. of fuming sulphuric acid. The mixture was then heated in an Erlenmeyer flask to about 120° C. for one hour. After cooling, the solution was carefully diluted with distilled water to about 60 ml. The indicator solution was then filtered before using, in a sintered glass crucible. About six to eight drops of 1% indicator were used in a determination. The percentage was calculated on the basis of indigotin, and not indigo tetrasulfonate. The color change is from yellow in dilute titanous solutions to red at the titanous end point.

The potassium salts of the indigo sulfonic acids may be prepared. Clark¹ gives full details for the procedures of all four sulfonates. The monosulfonate is rather insoluble for use as an indicator, especially in the presence of other salts. Clark's purification process depends mainly upon a series of recrystallizations, and the final products were tested by quantitative analysis of the elements. The potassium salts of the indigo sulfonates are very hygroscopic when dried at temperatures around 120° C. They are usually dried at 85° C. for an hour and bottled.



1 Studies on Oxid.-Redn., United States Public Health Dept., Reprint no. 848, 1923.

The first part of the paper discusses the importance of maintaining accurate records of all transactions. It is essential for the business to have a clear and concise record of all income and expenses. This will allow the business to track its financial performance over time and identify areas for improvement. The second part of the paper discusses the importance of maintaining accurate records of all assets and liabilities. This will allow the business to track its net worth over time and identify areas for improvement. The third part of the paper discusses the importance of maintaining accurate records of all taxes paid. This will allow the business to track its tax liability over time and identify areas for improvement. The fourth part of the paper discusses the importance of maintaining accurate records of all debts. This will allow the business to track its debt liability over time and identify areas for improvement. The fifth part of the paper discusses the importance of maintaining accurate records of all equity. This will allow the business to track its equity over time and identify areas for improvement. The sixth part of the paper discusses the importance of maintaining accurate records of all other financial information. This will allow the business to track its overall financial performance over time and identify areas for improvement.

The final part of the paper discusses the importance of maintaining accurate records of all other financial information. This will allow the business to track its overall financial performance over time and identify areas for improvement. The final part of the paper discusses the importance of maintaining accurate records of all other financial information. This will allow the business to track its overall financial performance over time and identify areas for improvement.

As can be seen from the indigo formula, the first three sulfonic acids of indigo have the possibility of several isomers. Vorländer and Schubart (1901) and Schubart (1902) synthesized, from intermediate products in which the position of the sulfonic acid was known, isomeric disulfonates of indigo. According to the above formula, they would be the 66' disulfonic acid and the 55' disulfonic acid of indigo. It was found that indigo carmine, as prepared by a sulfonation process, corresponded to the 55' disulfonic acid. A simple test may be made in order to determine which product one has. The 66' disulfonate gives no precipitate in dilute solutions with barium chloride, and a precipitate formed with basic lead acetate is soluble in excess of the precipitant. The 55' disulfonate gives a precipitate with barium chloride, and the precipitate with basic lead acetate is insoluble in an excess of the precipitant. Grandmougin (1909, 1921) points out that sulfonation occurs successively, first in the two positions, five para to the =NH of the indole nucleus, and next in the positions, seven ortho to the =NH group.

The positions of the sulfonic acid groups on the basis of the work of Vorländer, Schubart, and Grandmougin are as follows: (1) "mono," 5; (2) "di," 55'; (3) "tri," 55'7; (4) "tetra," 55'77'.

With the increase in sulfonation, the colors of the dilute solutions shift from an apparently ^{pure} blue to a decided reddish color. Both this shift and a decrease of specific absorption are shown.

Sullivan, Cohen, and Clark¹ in their Studies on Oxidation-Reduction, have given the oxidation and reduction potentials of the various indigo sulfonates. All measurements were made at 30° C. The meaning of the symbols used is as follows:

E_h = Observed reduction electrode potentials converted to hydrogen standard.

E_o^1 = The E_h value of a system of equal parts of total oxidant and of total reductant at constant pH.

π_h = Observed hydrogen electrode measurements.

E_o = E_o^1 at pH equals 0 or the hypothetical normal potential of a system.

TABLE VI*

ELECTRODE POTENTIALS OF MIXTURES OF INDIGO TRISULFONATE

AND THE REDUCTION PRODUCT

pH	Redn. cc.	Oxid. cc.	E_h	E_o^1	π_h	$E_o^1 - \pi_h = E_o$
1.419	7	3	+0.2351	+0.2462		
	5	5	0.2465	0.2465		
	3	7	0.2581	0.2470		
	5	5	0.2464	0.2464		
				0.2465	-0.0853	+0.3318
1.419	7	3	0.2347	0.2458		
	6	4	0.2414	0.2467		
	5	5	0.2464	0.2464		
	4	6	0.2523	0.2470		
	3	7	0.2579	0.2468		
				0.2465	-0.0853	0.3318
2.035	7	3	0.1988	0.2099		
	5	5	0.2097	0.2097		
	4	6	0.2152	0.2099		
	3	7	0.2212	0.2101		
				0.2099	-0.1223	0.3322
5.198	5	5	0.0199	0.0199		
	5	5	0.0200	0.0200		
				0.0200	-0.3124	0.3324
				(average) E_o		0.3321

* (Redn. and oxid. solutions are equal concentrations.)

TABLE VII¹

ELECTRODE POTENTIALS OF MIXTURES OF INDIGO MONOSULFONATE
AND THE REDUCTION PRODUCT,
EACH SOLUTION AT THE SAME CONCENTRATION

pH	Redn. cc.	Oxid. cc.	E_h	E_o^1	π_h	$E_o^1 - \pi_h = E_o$
2.034	5	5	+0.1390	+0.1390	-0.1222	0.2612
5.150	6	4	-0.0515	-0.0464		
	6	4	-0.0537	-0.0486		
	5	5	-0.0476	-0.0476		
	4	6	-0.0425	-0.0476		
				-0.0476	-0.3095	0.2619
8.694	5	5	-0.2083	-0.2083	-0.5225	
				average E_o		= 0.2616

TABLE VIII

POTENTIALS OF MIXTURES OF INDIGO DISULFONATE WITH THE REDUCTION PRODUCT
OF EACH SOLUTION BEING EQUAL IN CONCENTRATION

pH	reductant	oxidant	E_h	E_o^1	π_h	E_o
1.420	7 cc.	3 cc.	+0.1944	+0.2055		
	5	5	0.2053	0.2053		
	3	7	0.2162	0.2051		
				0.2053	-0.0854	0.2907
2.035	7	3	+0.1575	+0.1686		
	5	5	0.1685	0.1685		
	3	7	0.1798	0.1687		
				0.1686	-0.1223	0.2909
4.558	7	3	+0.0053	+0.0164		
	5	5	0.0164	0.0164		
	3	7	0.0277	0.0166		
				0.0165	-0.2740	0.2905
					average E_o	= 0.2907

¹ Tables Vi and VII were taken from U. S. Public Health Reports, reprint No. 848. 1923.

TABLE IX

POTENTIALS OF MIXTURES OF INDIGO TETRASULFONATE AND REDUCTION PRODUCT,
EACH BEING EQUAL IN CONCENTRATION

pH	reductant	oxidant	E_h	E_o^1	π_h	E_o
1.124	7 cc.	3 cc.	0.2874	0.2985		
	5	5	0.2985	0.2985		
	3	7	0.3095	0.2984		
				0.2985	-0.0676	0.3661
	7	3	0.2694	0.2805		
	5	5	0.2797	0.2797		
				0.2801	-0.0853	0.3654
	5	5	0.1914	0.1914		
	5	10	0.2005	0.1914		
				0.1914	-0.1693	0.3607
3.370	5	5	0.1608	0.1608	-0.2025	0.3633
2.811	5	5	0.1921	0.1921		
	3	7	0.2032	0.1921		
				0.1921	-0.1689	0.3610
					average E_o	= 0.3649

SUMMARY OF E_o VALUES FOR INDIGO SULFONATES

monosulfonate	=	0.2616
disulfonate	=	0.2907
trisulfonate	=	0.3321
tetrasulfonate	=	0.3649

Most of Clark's work has been done at relatively low acid concentrations. The determinations in this paper have been carried out in acid concentrations between 1.0 N and 7.2 N. Equation (10) has already been derived on page 32 of this report for the effect of acid concentration on the oxidation-reduction value of the indigo system.

$$E_h = E_o + \left[\frac{RT}{2F} \right] \ln \left| K_1 [H^+] + [H^+]^2 \right| \quad (10)$$

(Since the quantity, $K_1 [H^+]$, will be of the order of 10^{-7} and 10^{-8} , it is also neglected.)

Then

$$E_h = E_o + \left[\frac{RT}{2F} \right] \ln [H^+]^2 \quad (11)$$

or

$$E_h = E_o + \left[\frac{RT}{F} \right] \ln [H^+] \quad (12)$$

at 30° C.

$$E_h = E_o + 0.06 \text{ Log } [H^+] \quad (13)$$

Now, using the equation (13) and the E_o values for the various indigo sulfonates, the corresponding E_h values may be calculated. These are shown in TABLE X.

TABLE X

E_h VALUES

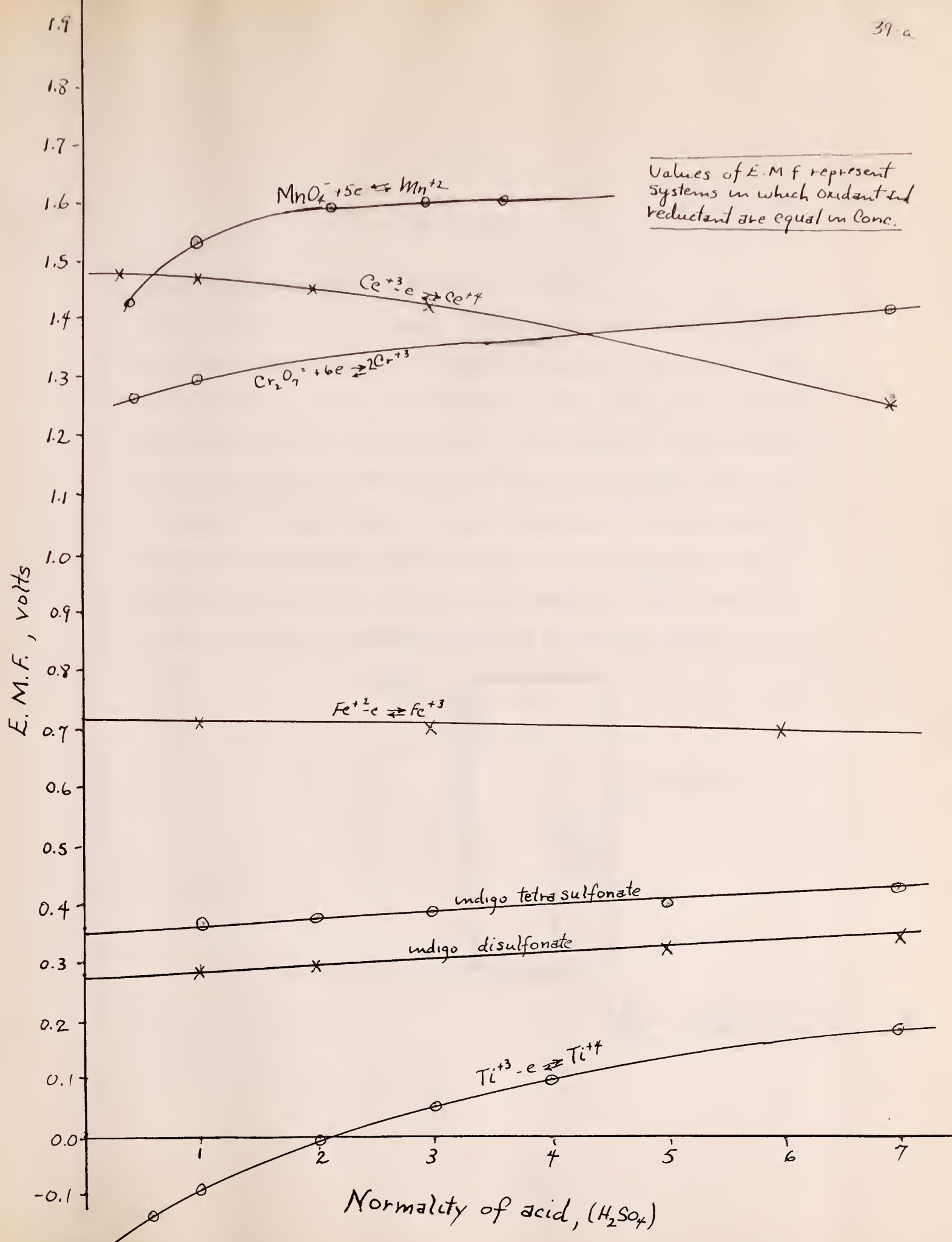
Sulfonates of Indigo	1 N acid = E_o value	2 N acid	3 N acid	5 N acid	7 N acid
mono-	0.2616	0.2797	0.2892	0.3035	0.3123
di-	0.2907	0.3088	0.3193	0.3326	0.3414
tri-	0.3321	0.3502	0.3607	0.3740	0.3828
tetra-	0.3649	0.3830	0.3935	0.4068	0.4156

The acid concentration does not affect the indicator system alone.

The acid concentration more or less affects practically all oxidation-reduction systems. The following graphs show most of the systems concerned in this report, and their relation to the hydrogen ion concentration.

Little will be said about the changes in oxidation-reduction potentials which are affected by different acids, because all the determinations were made in sulphuric acid solutions.





CHAPTER IV

EXPERIMENTAL

A. Preparation and storage of standard solutions:

Standard solutions of potassium permanganate, ceric sulfate, potassium dichromate, and ferric chloride were prepared and standardized. The usual precautions were taken in preparing the permanganate. Distilled water was used in all preparations. The permanganate was filtered by suction through a sintered glass crucible, after having stood on the steam bath for twelve hours. Figure 3 shows how the permanganate was stored so as to protect it from dust, and to eliminate opening and pouring the solution throughout the research. Cerium was stored likewise, but the dichromate was kept in an ordinary glass-stoppered bottle.

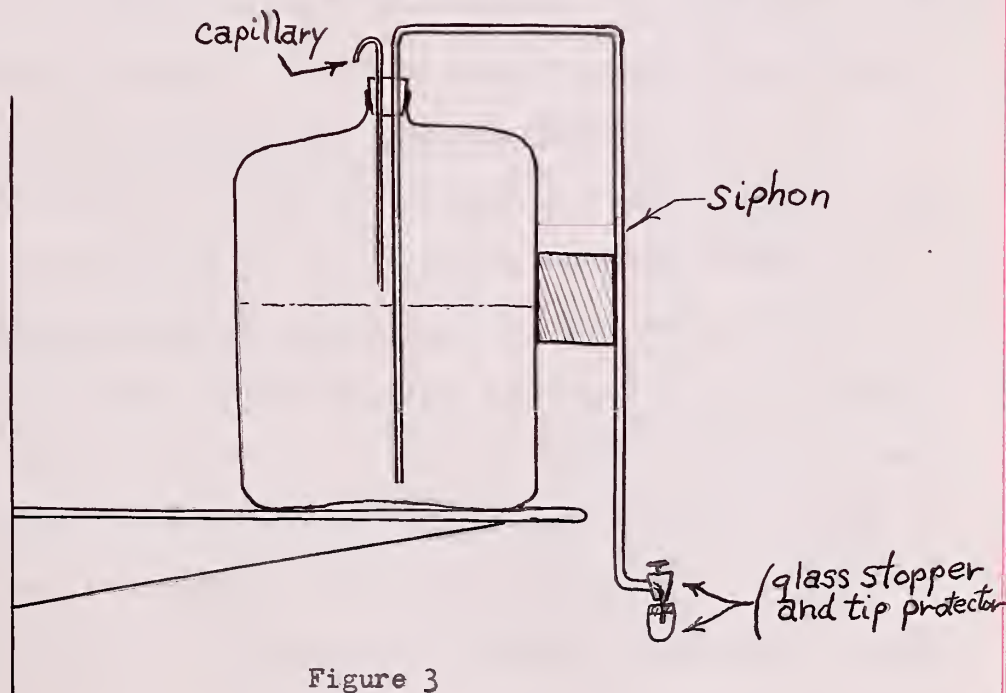


Figure 3

Cerium was prepared from anhydrous ceric sulfate, as supplied by the G. Frederick Smith Chemical Company. The permanganate and dichromate were prepared from Baker's C. P. reagents. Although the ceric sulfate was probably phosphate-free, it was allowed to stand ten days, and then was filtered. Sulphuric acid was used to keep the cerium in solution.

B. Standardization of solutions:

Pure sodium oxalate (factor of purity = 100.01) was used in the standardization of the permanganate. The method used was exactly as described in Kolthoff and Sandell's Quantitative Inorganic Analysis, page 564. The results of all the standardizations have been tabulated together on the following page.

Pure arsenious oxide (factor of purity = 99.83) was used in the standardization of the ceric sulfate solution. Three drops of osmic acid (0.01 M OsO_4 in $1 \text{ N H}_2\text{SO}_4$) was used as a catalyst, and one drop of ferrous-phenanthroline as indicator. The method used was exactly as described in Kolthoff and Sandell's Quantitative Inorganic Analysis, page 582.

The ferric chloride solution was standardized against standard permanganate and gravimetrically. In the former procedure, Kolthoff and Sandell's Quantitative Inorganic Analysis, page 572, was used again as reference. The stannous chloride solution was acidified with sulfuric acid instead of hydrochloric acid. Also, the solution titrated was acidified with sulfuric acid instead of the hydrochloric acid. The only chloride in the solution was then furnished by the ferric chloride and stannous chloride salts. The Zimmerman-Reinhardt solution was, neverthe-

less, used as specified. The gravimetric procedure was quite simple because of the absence of all interfering ions, except chloride ion. The iron was precipitated with ammonium, washed free of chloride ion, and ignited with the usual precautions.

In using titanium hydride as a reducing agent, the first problem presented was that of finding an effective method to put the hydride into solution. This would release nascent hydrogen and titanous ions which would reduce the iron to the ferrous condition. Dilute acids, even when heated, seemed to have little effect on the hydride. When a little water, however, was added to a mixture of titanium hydride and concentrated sulfuric acid, the heat generated and the presence of the water caused the hydrogen to evolve so rapidly that care had to be taken to keep the solution from foaming and splattering out. It was found that approximately 12 M or 24 N sulfuric acid at 120° - 140° C. caused the extremely rapid evolution of hydrogen. The solution of the hydride under these conditions was so fast that in a quantitative determination, there was too much danger from splattering. Furthermore, it was found that under the above conditions, the hydrogen was expelled so quickly that the reducing action of the nascent hydrogen was wasted. (See Table IV, page 27 of this report.) In reducing iron with titanium hydride, the following procedure was found to be most effective:

After solution of the iron sample by hydrochloric acid or nitric acid, the latter two acids are removed by heating to dryness or to sulphur trioxide fumes in the presence of 5-10 ml. of concentrated sulfuric acid.

In either case, a solid residue is formed. In the latter case, it is a white sulfate of iron. The solution is then diluted with water until the acid concentration is about 8-10 M. A small amount of titanium hydride is then added to the solution. The temperature should be somewhat less than 100° C. The temperature of the solution is raised slowly to about 120° - 140° C., during which time minute bubbles of nascent hydrogen will come off. Finally, a fairly rapid evolution of hydrogen is observed, and the solution will change from gray to light blue, and finally to violet. If no blue or violet color is observed, more titanium hydride must be added. With a little practice in adjusting the acid concentration and in selecting the proper amount of hydride, a reduction may be completed in two or three minutes. If the hydrogen is not expelled too rapidly, 25 mgs. of titanium hydride will reduce one milli-equivalent of iron, and in addition, will color the solution a distinct violet.

Powdered titanium metal was used for reduction, but was found to be slower and less efficient. Also, titanium metal, as stated before, is dangerous to handle because of its ease of oxidation at low temperatures and the great quantities of heat developed in oxidizing. (See Table III, page 26 of this report, for the reduction efficiency of titanium metal.)

In order to be sure that the hydride product did not contain iron or other interfering substances, and to locate the range of the oxidation-reduction potential so that a suitable indicator might be selected, several potentiometric titrations were made. Weighed portions of standard ferric chloride solution were taken from a weight burette for the determinations.

The titanium and iron were titrated with standard permanganate solution.

The potentiometric apparatus used throughout this research was set up as follows:

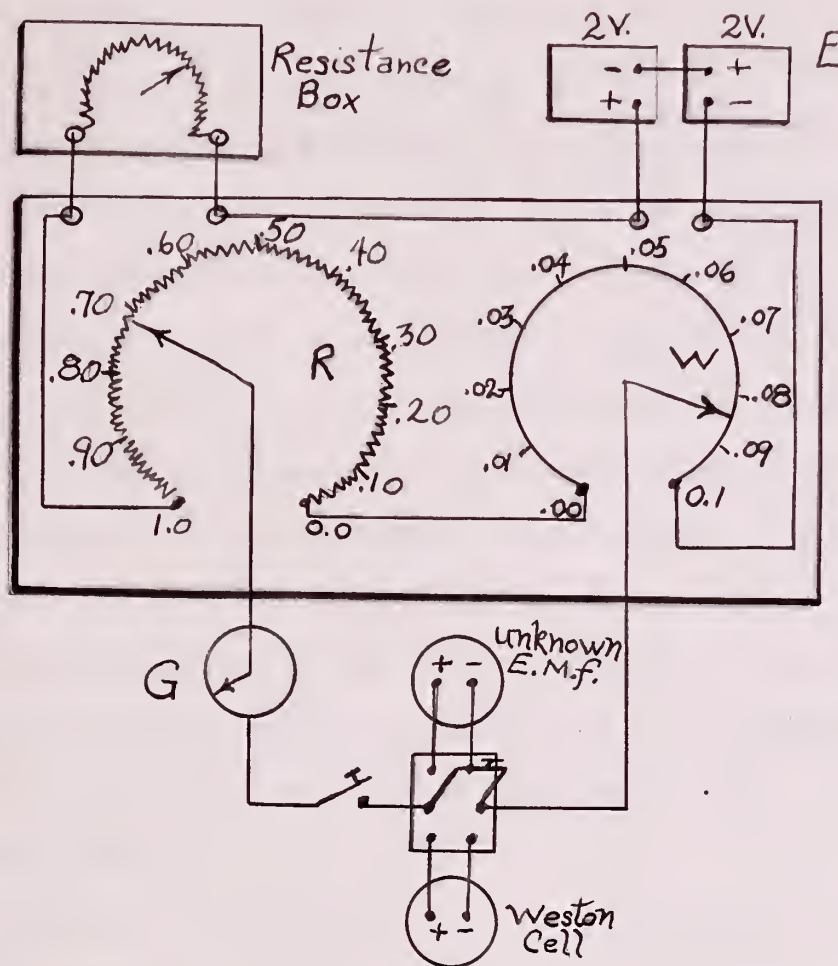


Figure 4

In Figure 4, E represents a constant electromotive force of approximately four volts. Two Willard cells connected in series proved to be a suitable source for electromotive force E. It is important that E furnish a constant electromotive force for long periods of time, so that steady readings can be obtained on the potentiometer. The potentiometer is made

up of two coils in series, R and W, each coil being divided into a number of parts. Coil R is divided into fifteen parts which each represent the same unit of resistance. Coil W is divided into ten parts so that each part has a resistance one-tenth the resistance of any part of coil R. The constant electromotive force furnished by the battery E decreases across the coil R by a certain unknown unit. There is, likewise, a potential drop across coil W, which is equal to one of the unknown unit drops in coil R. The value of the unit drop in potential across the coils may now be increased or decreased by increasing or decreasing the electromotive force from cell E. This is accomplished by a variable resistance, which is placed in series with E. There is, of course, a maximum increase which is dependent upon the value (volts) of the electromotive force furnished by E. In potentiometric work, the unit drop of potential across the coils is adjusted so that the numbers represent volts. This adjustment can be made by use of a standard cell which furnishes a steady and known electromotive force. A Weston cell (1.0183 v. at 20° C.) was used in this work. The temperature was approximately 30° C.

$$\text{Electromotive force at } 30^{\circ} \text{ C.} = 1.0183 - (0.0000406)t^{\circ} (30^{\circ} - 20^{\circ}) = 1.0183 - 0.000406.$$

$$\text{Electromotive force at } 30^{\circ} = 1.0179 \text{ volts.}$$

The Weston cell was connected (Figure 4) so as to oppose the electromotive force of battery E. The potentiometer contacts were set so as to read 1.0179 on the dials, and the electromotive force of the battery was adjusted by the resistance box so that no current flowed: i. e., the

The first part of the paper discusses the importance of understanding the underlying mechanisms of the observed phenomena. It is argued that a comprehensive understanding of the system is essential for developing effective interventions. The second part of the paper presents a detailed analysis of the data, highlighting the key findings and their implications. The third part of the paper discusses the limitations of the study and suggests directions for future research.

The results of the study indicate that there is a significant relationship between the variables under investigation. This finding is consistent with previous research in the field. The study also identified several factors that influence the outcome, which have important implications for practice. The findings suggest that a multi-faceted approach is needed to address the issue effectively. The study's limitations include a relatively small sample size and a cross-sectional design, which may limit the generalizability of the findings.

In conclusion, the study provides valuable insights into the complex nature of the phenomenon being studied. The findings have important implications for both theory and practice. Further research is needed to explore the underlying mechanisms and to develop more targeted interventions. The study's limitations and strengths are discussed, and directions for future research are suggested.

system was balanced. A galvanometer placed in series in the system indicated the flow of the current. If an appreciable current is drawn from the cell, some of the electrical energy will be wasted, as heat and the maximum work cannot be obtained. Therefore, the system is in equilibrium only when an infinitesimal current flows, as indicated by the galvanometer when the pointer fails to deflect. The system was tested by completing the circuit with a tap key for only a few seconds. A prolonged flow of current may harm the standard cell, and adjustments may be made without danger to the instruments. When the system is balanced under the above conditions, the numbers on the coil contacts represent the true voltage. Now, by means of a double throw switch, the system can be made to oppose another electromotive force. This electromotive force was furnished by a cell made as shown in Figure 5.

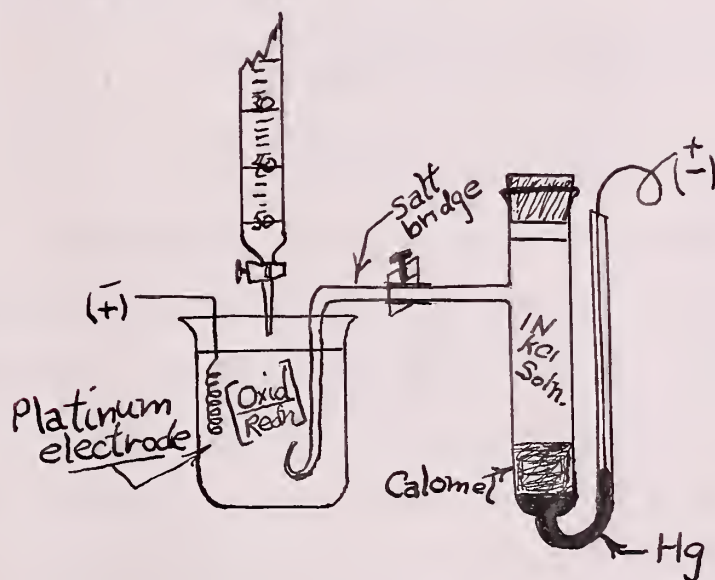


Figure 5

A platinum wire constitutes one electrode and a normal calomel reference electrode, the other. The solution is titrated, and the potential of the system is obtained by balancing the currents and reading the voltage directly from the potentiometer. (A series of potential readings and corresponding volumes of standard solution were thus obtained and graphed.) The potentiometer calibration may be re-checked at any time by throwing the double throw switch so as to place the Weston cell in the circuit.

The normal calomel cell was checked against a hydrogen electrode in standard hydrochloric acid solution. The formula for the hydrogen electrode against the normal calomel at 25° C. is as follows:

(the pH of the hydrochloric solutions were 1.22 and 0.92)

$$E = 0.059 \log \frac{1}{a_H} + 0.281$$

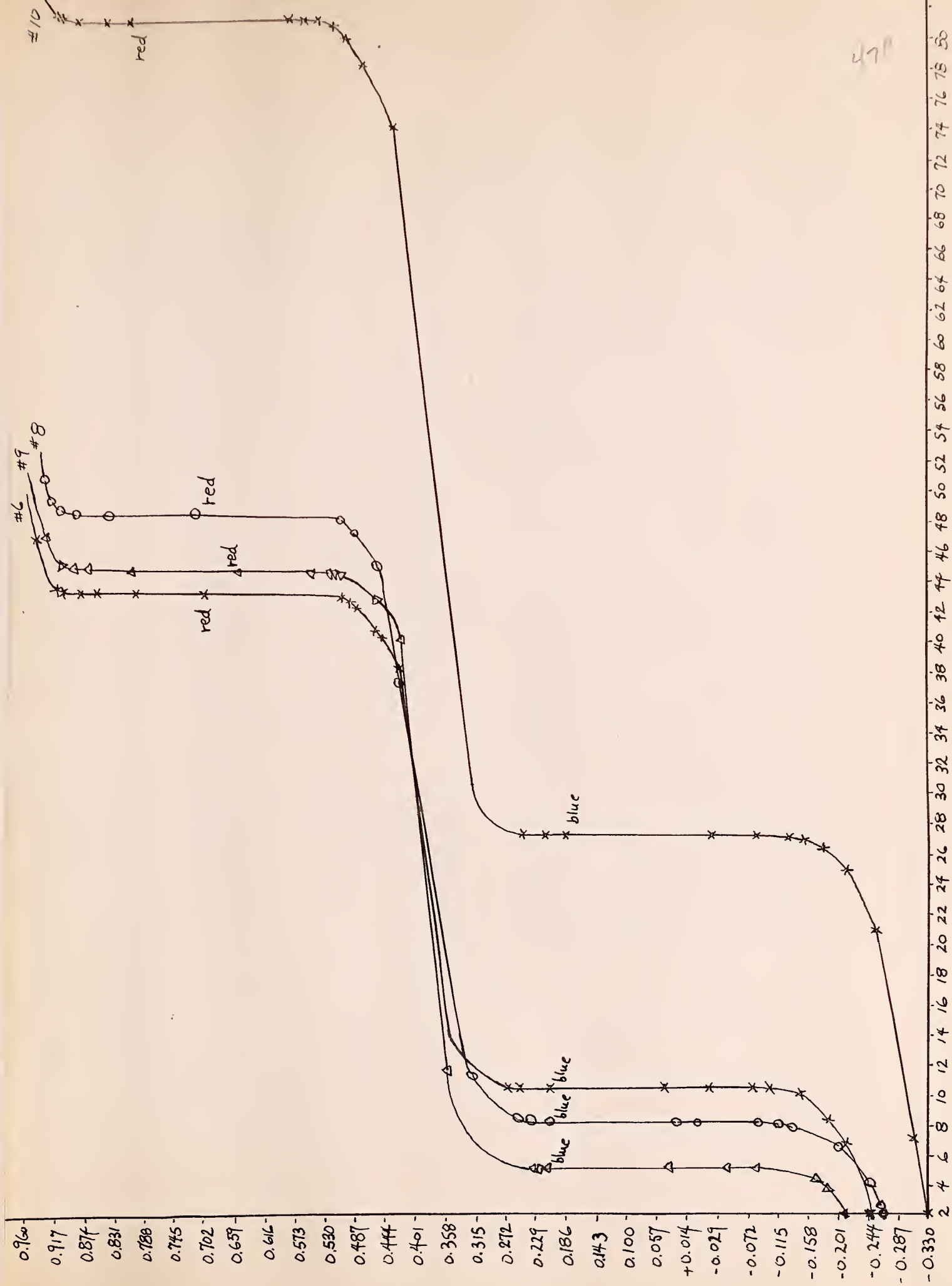
$$(1) \quad E = 0.059 (1.22) + 0.281 = 0.346$$

E observed was = 0.342

$$(2) \quad E = 0.059 (0.92) + 0.281 = 0.335$$

E observed was = 0.333

In obtaining the four potentiometric titration curves shown on the following page, titanium hydride was used for the reduction, as already described. Standard permanganate was used, and after each addition, the solution was stirred by hand before taking the potentiometer reading. The potentials were very stable after less than one minute of stirring. The titrations were all made at room temperature, 25° C., and in 1 N sulphuric acid. Samples of the standard iron solution were weighed by means of a weight burette. The results of TABLE XV were obtained for the per cent of iron in the solution.



ml. of 0.1219N. $KMnO_4$ solution

POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XV AND GRAPH 1

Sample #6

0.00 ml. KMnO_4	-0.245 v.	43.20.....	+0.445
5.30.....	-0.210	45.15.....	0.465
6.30.....	-0.195	45.95.....	0.480
8.25.....	-0.145	46.50.....	0.500
8.70.....	-0.100	46.60.....	0.710 pink
8.90.....	-0.090	46.65.....	0.840
9.00.....	-0.015	46.70.....	0.890
9.05.....	+0.040	46.80.....	0.900
9.10.....	+0.205 blue	47.85.....	0.915
9.20.....	+0.245	48.95.....	0.925
9.40.....	+0.255		
36.20.....	+0.415		
38.50.....	+0.440		
38.95.....	+0.445		
40.65.....	+0.465		
40.95.....	+0.480		
41.20.....	+0.490		
41.30.....	+0.700 pink		
41.40.....	+0.795		
41.50.....	+0.860		
41.60.....	+0.885		
41.70.....	+0.905		
41.80.....	+0.915		
45.00.....	+0.940		

Sample #9

0.00.....	-0.210
2.10.....	-0.185
2.85.....	-0.165
3.60.....	-0.085
3.65.....	-0.040
3.70.....	+0.035
3.75.....	0.205 blue
3.80.....	0.220
3.85.....	0.230
10.00.....	0.350
38.50.....	0.430
41.00.....	0.450
42.65.....	0.500
42.70.....	0.505
42.80.....	0.515
42.90.....	0.545
42.95.....	0.645
43.00.....	0.800 pink
43.10.....	0.875
43.15.....	0.895
43.20.....	0.900
45.00.....	0.930

Sample #8

0.00.....	-0.265
1.00.....	-0.255
3.20.....	-0.240
5.00.....	-0.205
6.10.....	-0.140
6.20.....	-0.120
6.40.....	-0.090
6.50.....	-0.010
6.60.....	+0.020
6.65.....	+0.205 blue
6.70.....	0.230
6.90.....	0.250
7.00.....	0.255
9.80.....	0.315
35.70.....	0.405

POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XV AND GRAPH 1 (CONT.)

Sample #10

0.00.....	-0.330	
5.75.....	-0.300	
19.60.....	-0.250	
23.40.....	-0.210	
24.70.....	-0.175	
25.10.....	-0.155	
25.25.....	-0.120	
25.40.....	-0.095	
25.45.....	-0.025	
25.50.....	0.180	blue
25.55.....	0.205	
25.80.....	0.235	
72.15.....	0.420	
76.25.....	0.450	
78.10.....	0.475	
79.00.....	0.505	
79.20.....	0.520	
79.30.....	0.540	
79.35.....	0.565	
79.40.....	0.640	
79.45.....	0.805	pink
79.50.....	0.850	
79.55.....	0.885	
79.60.....	0.900	
79.80.....	0.915	
82.00.....	0.950	

TABLE XI - A

Standardization of KMnO_4 solution with sodium oxalate (100.01% pure)

no.	ml. of KMnO_4	wt. of $\text{Na}_2\text{C}_2\text{O}_4$, gm.	normality of KMnO_4	
1	49.15	0.4018	0.1220	
2	26.25	0.2141	0.1217	July 22, 1942
3	19.75	0.1613	0.1219	
Average			0.1219	

TABLE XI - B

Check on normality of KMnO_4 made eight days later, using $\text{Na}_2\text{C}_2\text{O}_4$

no.	ml. of KMnO_4	wt. of $\text{Na}_2\text{C}_2\text{O}_4$, gm.	normality of KMnO_4	
1	17.80	0.1453	0.1218	
2	21.55	0.1757	0.1217	July 30, 1942
3	41.55	0.3393	0.1219	
Average			0.1218	

Normality of KMnO_4 used in calculations = 0.1219

TABLE XII

Standardization of $\text{Ce}(\text{SO}_4)_2$ with As_2O_3 (purity 99.83%)
(Osmic acid used as catalyst with o-phenthroline ferrous complex as indicator.)

no.	ml. of $\text{Ce}(\text{SO}_4)_2$	wt. of As_2O_3 , gms.	normality of $\text{Ce}(\text{SO}_4)_2$	
1	36.50	0.1555	0.08600	
2	37.65	0.1604	0.08600	
3	49.00	0.2089	0.08606	
4	58.95	0.2513	0.08605	July 28, 1942
5	56.45	0.2411	0.08614	
Average			0.08605	
(used in calculations)				

TABLE XIII - A

Standardization of a solution of ferric chloride, using the gravimetric procedure.

no.	wt. of solution, gms.	wt. of Fe_2O_3 ppt.	per cent of iron
63	6.5980	0.3028	3.210
64	5.9316	0.2725	3.213
66	4.2454	0.1252	3.216
67	4.6458	0.2134	3.212
Average			3.213

August 18, 1942

TABLE XIII - B

Standardization of ferric chloride solution with 0.1219 N potassium permanganate, reducing with SnCl_2 , taking the usual precautions, and using Zimmermann-Reinhardt solution.

no.	ml. of KMnO_4	wt. of solution, gms.	per cent of iron
2	21.00	4.4601	3.205
3	24.42	5.1939	3.200
4	27.00	5.7321	3.206
5	47.35	10.0439	3.209
Average			3.205

July 23, 1942

TABLE XIII - C

Check (made ten days later) on the per cent of iron, using the same procedure.

21	21.95	4.6548	3.210
22	30.75	6.5144	3.213
24	32.95	6.9813	3.213
Average			3.212

July 30, 1942

TABLE XIV - A

Standardization of potassium dichromate with standard iron solution, stannous chloride used as reducing agent, and sodium diphenylamine sulfonate as indicator in the presence of phosphoric acid. (Per cent of iron in solution taken as 3.212.)

no.	ml. of $K_2Cr_2O_7$	wt. of iron solution, gms.	normality of $K_2Cr_2O_7$	
39	23.80	7.0617	0.1707	
40	31.15	9.2355	0.1706	August 3,
41	19.50	5.7754	0.1704	1942
Average			0.1706	

TABLE XIV - B

Normality of potassium dichromate, as calculated from the weight of dried C. P. salt used. (M. w. = 294.21.)

wt. of pure dried $K_2Cr_2O_7$	vol. of final solution at 20° C.	normality of $K_2Cr_2O_7$
17.7308 gms.	2119.50 ml ✓	0.1706

TABLE XV

Using titanium hydride in place of $SnCl_2$ and 0.1219 N potassium permanganate, determining the two end points potentiometrically.

no.	wt. of iron solution, gms.	ml. of $KMnO_4$	per cent of iron
6	6.8228	32.20	3.213
8	8.4948	39.95	3.201
9	8.3291	39.25	3.208
10	11.4579	53.95	3.205
Average			3.209
Per cent of iron obtained using Zimmermann-Reinhardt method = 3.205			

The first part of the paper discusses the importance of the study and the objectives of the research. It also mentions the scope of the study and the limitations of the study.

The second part of the paper discusses the methodology used in the study. It mentions the data sources and the data collection methods used in the study.

The third part of the paper discusses the results of the study. It mentions the findings of the study and the conclusions drawn from the study.

The fourth part of the paper discusses the implications of the study. It mentions the practical implications of the study and the theoretical implications of the study.

The fifth part of the paper discusses the limitations of the study. It mentions the limitations of the study and the limitations of the study.

The sixth part of the paper discusses the conclusions of the study. It mentions the conclusions of the study and the conclusions of the study.

The seventh part of the paper discusses the future research. It mentions the future research and the future research.

The results in TABLE XV have been compared with the per cent of iron obtained in TABLE XIII - B, using the usual Zimmermann-Reinhardt method. These figures are somewhat low, compared with later results, as shown in TABLES XIII - A and XIII - B. The solutions of iron for samples 2-10 inclusive were weighted out on the same day, and the determinations carried out on the two successive days indicated. The laboratory temperature was high, about $30^{\circ}\text{C}.$, and the glass stopper was not greased until the results in TABLE XVI were obtained on July 29, which were high, indicating that water was slowly being distilled from the bottle. The two checks made about eighteen days apart on the iron solution, and shown in TABLES XIII - A and XIII - C, indicate that the per cent of iron remained constant after precautions were taken to see that the stopper was well sealed.

The potentiometric graphs show that a break in potential of 100 m. v. or more is obtained at the titanium end point, followed by a similar break at the permanganate end point. The reaction was carried out in approximately 2 N sulfuric acid solution. No difficulty was encountered throughout.

TABLE XVI

Determination of iron in standard solution, using indigo disulfonate in place of the potentiometer for the first end point, and the red coloration of permanganate for the second end point.

no.	ml. of KMnO_4	wt. of iron solution	per cent of iron	
16	21.30	4.5144	3.212	
17	23.45	4.9561	3.221	
18	44.15	9.3852	3.202	July 29, 1942
19	24.15	5.0973	3.225	
20	25.50	5.4016	3.213	
Average			3.215	
Per cent of iron found by Zimmerman-Reinhardt method =				3.212

1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that proper record-keeping is essential for the transparency and accountability of the organization. This section also outlines the various methods used to collect and analyze data, ensuring that the information is reliable and up-to-date.

2. The second part of the document focuses on the financial aspects of the organization. It provides a detailed overview of the budget, including the projected income and expenses for the upcoming year. This section also discusses the various financial risks and how they are being managed to ensure the organization's financial stability.

3. The third part of the document addresses the operational aspects of the organization. It describes the various processes and procedures that are in place to ensure the efficient and effective delivery of services. This section also discusses the various challenges that the organization is facing and how they are being addressed.

4. The fourth part of the document discusses the human resources aspect of the organization. It provides an overview of the current staff levels and the various training and development programs that are in place. This section also discusses the various challenges that the organization is facing in terms of recruitment and retention of staff.

5. The fifth part of the document discusses the legal and regulatory aspects of the organization. It provides an overview of the various laws and regulations that the organization is subject to and how they are being managed. This section also discusses the various challenges that the organization is facing in terms of compliance with these laws and regulations.

Appendix A: Financial Data	
Year	Amount
2018	120,000
2019	150,000
2020	180,000
2021	200,000
2022	220,000

Appendix B: Operational Data	
Category	Value
Production	10,000 units
Quality Control	95% pass rate
Customer Satisfaction	4.5/5 stars
Employee Turnover	15%
Training Hours	500 hours

The results in TABLE XVI were obtained without the aid of a potentiometer, and the first end point with indigo disulfonate was very distinct and sharp, if the solution was titrated slowly and kept well stirred near the end point. If the titration is carried out too rapidly at the end point, indigo disulfonate turns blue ahead of time, and the reverse reaction to the colorless leuco-compound is a little slower. Another point which should be kept in mind is that excessive stirring of the solution near the titanium end point facilitates the reaction of atmospheric oxygen with titanous ions, and in some cases, the indigo will turn blue without the addition of permanganate. If this occurs, the end point is just as valid as that obtained by the addition of permanganate. Also, after reduction of the iron solution in sulfuric acid, a purple color may be observed before dilution, and may then disappear after dilution. If indigo remains blue in such a solution, one can safely assume that dissolved oxygen in the water oxidized all the titanous ions to titanic ions. Similar aeration procedures as described by Troug and Pearson and Axt and Le Roy have been discussed on page 9 and 10 and 16, respectively.

The blue color of the indigo fortunately disappears well before the permanganate end point is obtained. The addition of 5 cc. of phosphoric acid near the second end point enables one to have a perfectly colorless solution at the permanganate end point. A white precipitate is formed with titanic ions in about fifteen to twenty minutes. This allowed ample time to find the end point. The iron solution was checked immediately after the results in TABLE XVI were obtained by the Zimmermann-Reinhardt method, and that result is compared with those in the table.

The determinations shown in TABLE XVII were made with standard ceric sulfate solution in place of permanganate. The reduction was carried out as before with titanium hydride and the first end point found with indigo disulfonate and the second with ortho-phenthroline ferrous complex. Osmic acid was used as catalyzer in all the ceric analyses. The reaction was carried out in approximately 1 N sulfuric acid medium, and the indigo remaining from the first end point was completely destroyed before the second end point was reached.

TABLE XVII - A (1 N sulfuric acid)

no.	ml. of 0.08605 <u>N</u> $\text{Ce}(\text{SO}_4)_2$	wt. of iron solution, gms.	per cent of iron
27	37.70	5.6839	3.188
28	38.90	5.8756	3.182
29	45.65	6.8900	3.184
30	40.30	6.0765	3.187
32	31.85	4.7925	3.194
Average			3.187
Per cent of iron, using Zimmermann-Reinhardt method = 3.212			

In TABLE XVII - B, the acid concentration was increased to about 2-6 N in sulfuric acid. Potentiometric curves are shown for the asterisk marked determinations. The potentiometer showed the largest breaks in the higher acid concentrations. The color change of the indicators, however, was affected very little, being very sharp in 1 N to 6 N acid.

Introduction

The purpose of this study is to investigate the effects of various factors on the performance of a system. The factors being studied are the number of users, the amount of data, and the type of hardware. The results of the study will be presented in a series of tables and graphs. The first table shows the results of the first experiment, and the second table shows the results of the second experiment. The graphs show the relationship between the factors and the performance of the system. The first graph shows the relationship between the number of users and the performance of the system, and the second graph shows the relationship between the amount of data and the performance of the system.

Methodology

The methodology used in this study is a combination of experimental and analytical methods. The experimental method involves the use of a test system to measure the performance of the system under various conditions. The analytical method involves the use of mathematical models to predict the performance of the system under various conditions.



The results of the study show that the performance of the system is significantly affected by the number of users and the amount of data. The performance of the system decreases as the number of users increases and as the amount of data increases. The performance of the system is not significantly affected by the type of hardware used.

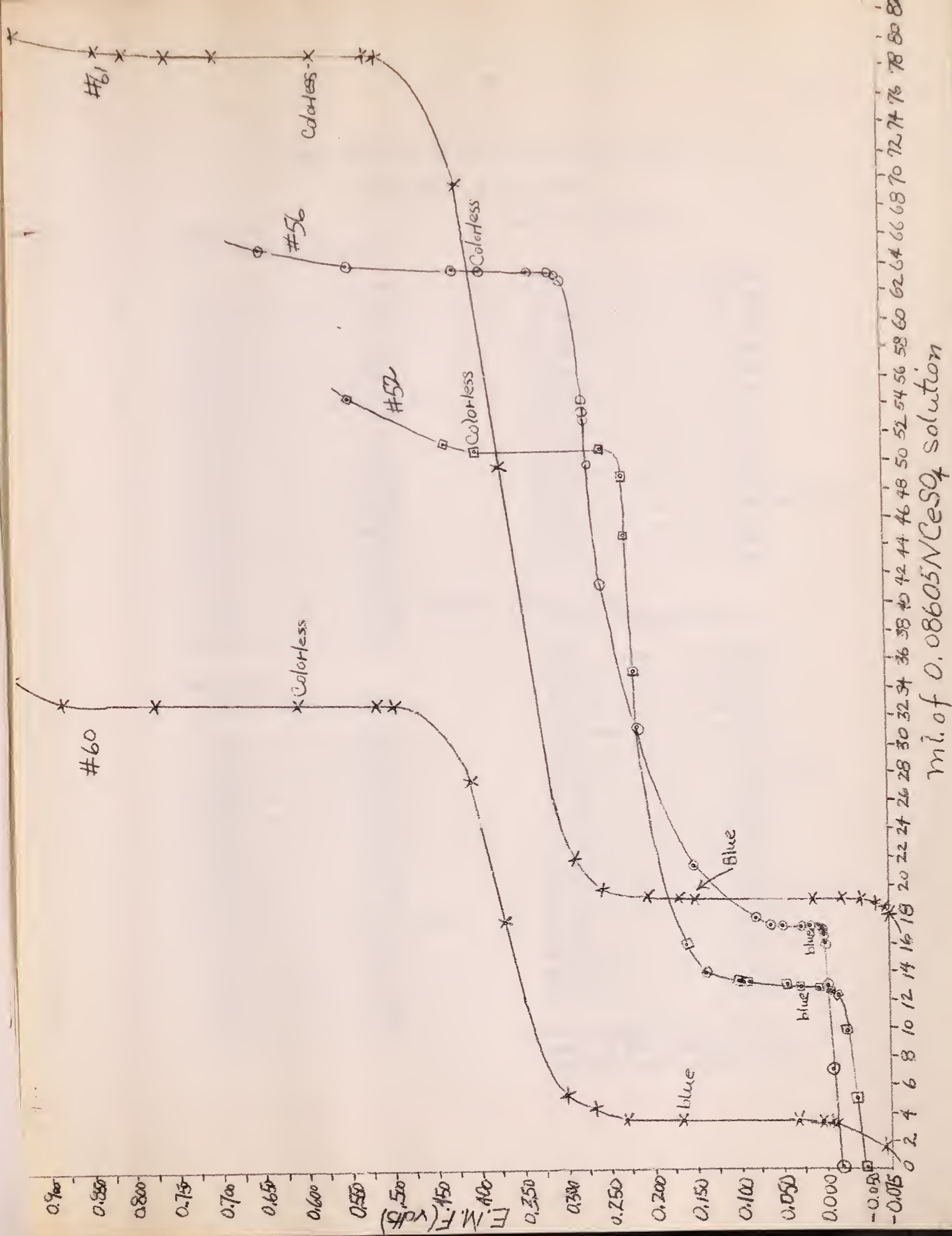
Conclusion

In conclusion, the study has shown that the performance of the system is significantly affected by the number of users and the amount of data. The performance of the system decreases as the number of users increases and as the amount of data increases. The performance of the system is not significantly affected by the type of hardware used. These results have important implications for the design and use of the system. The system should be designed to handle a large number of users and a large amount of data. The system should also be designed to be able to handle different types of hardware.

TABLE XVII - B

no.	ml. of 0.08605 $\text{Ce}(\text{SO}_4)_2$	wt. of iron solution, gms.	per cent of iron
49	38.20	5.7454	3.195
50	45.70	6.8681	3.198
51	34.00	5.1041	3.201
52*	38.20	5.7466	3.195
53	32.00	4.7780	3.204
56*	46.45	6.9631	3.206
60*	29.80	4.4773	3.199
61*	60.70	9.1192	3.199
Average			3.200
Per cent, using Zimmermann-Reinhardt method = 3.212			

Potassium dichromate was also used as a standard oxidizing agent with little change in the procedure. Potentiometric graphs were made with the indicators to observe the breaks in relation to the color changes. Good potentiometric breaks were obtained with dichromate only at acidities of 6-7 N. Sulfuric acid was used. Sodium diphenylamine sulfonate with phosphoric acid was used for the iron end point indicator. In sample 62, indigo tetrasulfonate was used, while in the others the disulfonate indicated when the titanium was completely oxidized. The tetrasulfonate turns red instead of blue at the titanium end point. The formation of green chromic ions tends to make the blue end point difficult to see, although no difficulty was experienced when the excess titanous ions were not too great so as to require large amounts of potassium dichromate for oxidation. Indigo disulfonate and indigo tetrasulfonate are not completely destroyed at the second end point, as they are with potassium permanganate and ceric sulfate. Fortunately, however, a good deal of the original indicator is destroyed, and the intensity of color is usually very light, but this, combined with



POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XVII - B AND GRAPH 3

Sample #52

(15 ml. H_2SO_4 /200 ml.)

0.00.....	-0.040	
5.00.....	-0.035	
10.00.....	-0.024	
12.50.....	-0.012	
12.80.....	-0.008	
12.85.....	-0.007	
12.90.....	+0.010	blue
12.95.....	0.030	
13.00.....	0.041	
13.10.....	0.092	
13.20.....	0.096	
14.00.....	0.133	
16.00.....	0.158	
35.50.....	0.220	
45.00.....	0.230	
49.10.....	0.232	
51.00.....	0.250	
51.10.....	0.395	colorless
51.50.....	0.430	
55.00.....	0.568	

Sample #56

(15 ml. H_2SO_4 /200 ml.)

0.00.....	-0.018	
7.50.....	-0.008	
13.05.....	-0.002	
16.00.....	0.000	
16.20.....	+0.002	
16.40.....	0.003	
16.60.....	0.004	
16.70.....	0.006	
16.80.....	0.007	
17.00.....	0.008	
17.05.....	0.015	blue
17.15.....	0.023	
17.45.....	0.050	
17.70.....	0.063	
18.00.....	0.077	
21.50.....	0.152	
31.50.....	0.217	

Sample #56 (cont.)

41.50.....	+0.256	
50.00.....	0.265	
53.05.....	0.273	
53.30.....	0.274	
53.40.....	0.275	
53.45.....	0.275	
53.50.....	0.275	
54.00.....	0.275	
62.95.....	0.295	
63.20.....	0.300	
63.30.....	0.310	
63.45.....	0.335	
63.50.....	0.385	colorless
63.65.....	0.420	
64.00.....	0.535	
65.00.....	0.640	

Sample #60

(40 ml. H_2SO_4 /200 ml.)

0.00.....	-0.083	
1.40.....	-0.070	
3.15.....	-0.010	
3.20.....	-0.008	
3.30.....	+0.010	
3.35.....	0.035	
3.40.....	0.171	blue
3.55.....	0.230	
4.15.....	0.272	
5.35.....	0.302	
17.80.....	0.369	
27.95.....	0.412	
32.95.....	0.494	
33.20.....	0.515	colorless
33.25.....	0.605	
33.35.....	0.770	
33.80.....	0.880	
35.00.....	0.935	
37.00.....	0.965	

(Great improvement will be noted in #60 because of the increased acid concentration.)

POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XVII - B AND GRAPH 3 (CONT.)

Sample #61

(35 ml. H_2SO_4 /200 ml.)

0.00.....	-0.192	
16.00.....	-0.110	
17.50.....	-0.087	
18.00.....	-0.077	
18.15.....	-0.070	
18.20.....	-0.065	
18.40.....	-0.035	
18.45.....	-0.020	
18.50.....	-0.015	
18.55.....	0.150	blue
18.60.....	0.170	
18.70.....	0.210	
19.60.....	0.260	
22.00.....	0.290	
50.00.....	0.372	
70.00.....	0.417	
79.00.....	0.510	
79.20.....	0.520	
79.25.....	0.580	colorless
79.30.....	0.690	
79.35.....	0.750	
79.45.....	0.800	
79.55.....	0.830	
81.00.....	0.925	

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF CHEMISTRY
RESEARCH REPORT NO. 1000

BY J. H. GOLDSTEIN AND
R. L. SEXTON

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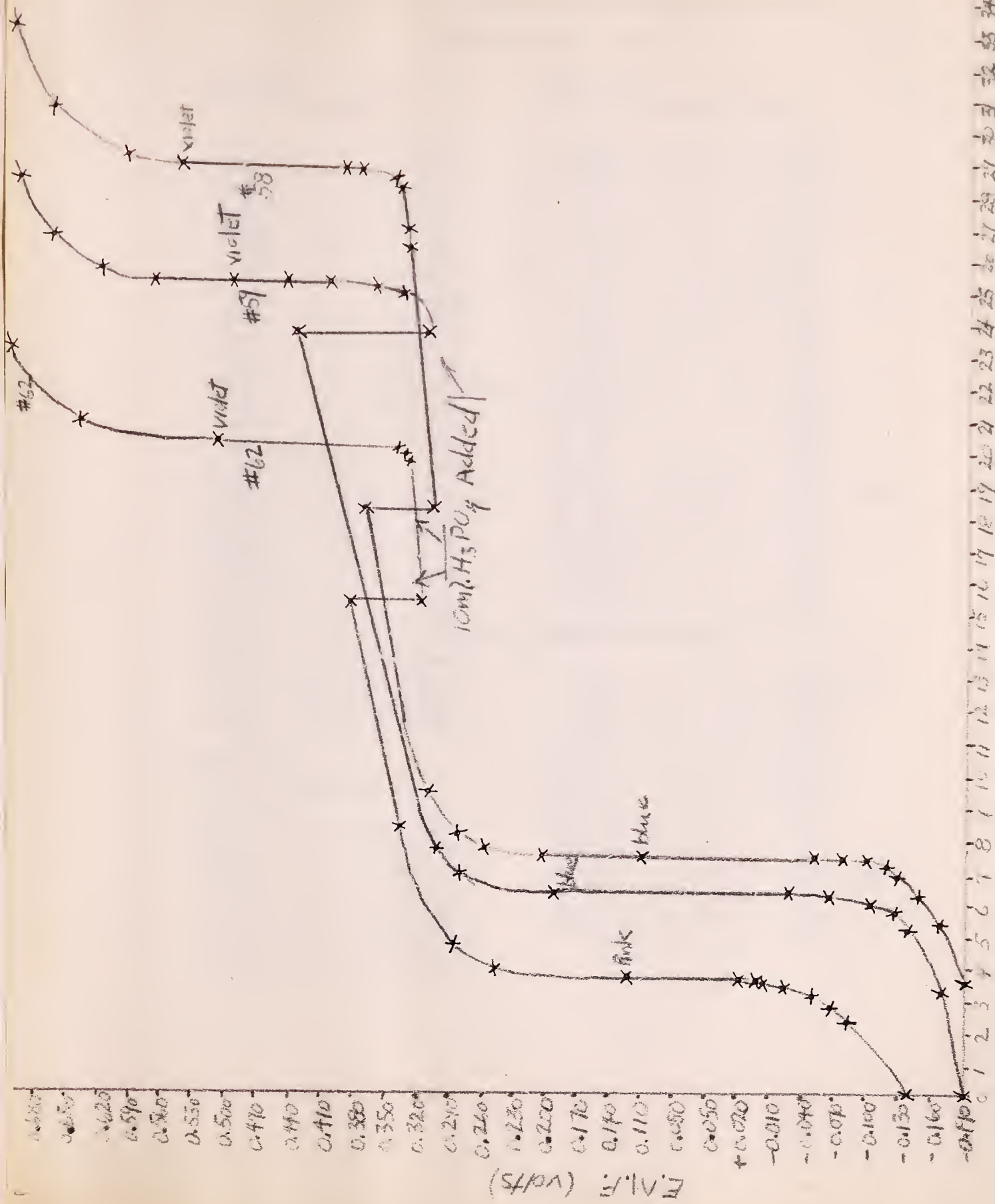
the green of the chromic ions, can make the second end point difficult to locate. It was found that, using a total of thirty milliliters of 0.1706 N potassium dichromate with 6-8 drops of either the di- or tetra-sulfonate of indigo, both end points could be seen in good light.

TABLE XVIII

Potassium dichromate, titanium hydride, indigo sulfonates, and sodium di-phenylamine sulfonate used in determining iron.

no.	ml. of 0.1706 N $K_2Cr_2O_7$	wt. of iron soln., gms.	per cent of iron
54	18.60	5.4953	3.224
55	18.65	5.5149	3.222
58*	21.60	6.4090	3.211
59*	18.90	5.6063	3.212
62*	16.55	4.9097	3.212
Average			3.216
Per cent of iron by Zimmermann-Reinhardt method = 3.212			

The determinations on the iron solution show that the indigo sulfonate indicators and titanium hydride are applicable to the determination of iron with an accuracy of 2 or 3 parts per thousand. A number of determinations have been made on the United States Bureau of Standards, sample no. 26, in order to find the best possible accuracy of the determination. Care was taken to be consistent in selecting the end points. The first end point was taken after the first drop of standard solution turned the indigo a permanent blue color. No addition was made to the first burette reading. The second reading was taken when the first drop or fraction turned the second indicator. The last drop or fraction of drop was subtracted from the second burette reading. This procedure was



ml. of 0.1706 N. $K_2Cr_2O_7$ solution



POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XVIII AND GRAPH 4

Sample #58

(40 ml. H_2SO_4 /200 ml.)

0.00.....	-0.218	
1.50.....	-0.210	
2.70.....	-0.200	
3.70.....	-0.190	
5.40.....	-0.166	
6.20.....	-0.147	
7.00.....	-0.125	
7.10.....	-0.115	
7.20.....	-0.099	
7.35.....	-0.077	
7.45.....	-0.051	
7.50.....	+0.110	blue
7.55.....	0.205	
7.80.....	0.260	
8.10.....	0.280	
9.30.....	0.313	
18.30.....	0.377	
18.30.....	0.306	
26.50.....	0.335	
27.00.....	0.339	
28.25.....	0.345	
28.50.....	0.350	
28.80.....	0.380	
28.95.....	0.395	violet
29.00.....	0.545	
29.30.....	0.600	
30.80.....	0.668	
33.20.....	0.702	

Sample #62

(40 ml. H_2SO_4 /200 ml.)

0.00.....	-0.140	
2.20.....	-0.082	
2.90.....	-0.065	
3.10.....	-0.050	
3.30.....	+0.023	
3.55.....	-0.005	
3.60.....	+0.002	
3.70.....	0.020	

Sample #59

(40 ml. H_2SO_4 /200 ml.)

0.00.....	-0.190	
3.20.....	-0.170	
5.20.....	-0.140	
5.75.....	-0.125	
6.00.....	-0.100	
6.25.....	-0.065	
6.35.....	-0.025	
6.40.....	+0.190	blue
7.00.....	0.280	
7.70.....	0.305	
23.80.....	0.440	
23.80.....	0.310	
24.95.....	0.340	
25.10.....	0.365	
25.20.....	0.410	
25.25.....	0.450	
25.30.....	0.500	violet
25.35.....	0.570	
25.70.....	0.623	
26.70.....	0.665	
28.50.....	0.695	
33.00.....	0.720	

Sample #62 (cont.)

3.75.....	+0.125	pink
4.00.....	0.250	
4.70.....	0.290	
8.50.....	0.342	
15.45.....	0.390	
15.45.....	0.320	
19.90.....	0.330	
20.00.....	0.335	
20.25.....	0.340	
20.30.....	0.510	violet
21.00.....	0.640	
23.20.....	0.710	
25.50.....	0.740	

also followed in standardizing the permanganate, ceric sulfate, and dichromate solutions.

TABLE XIX

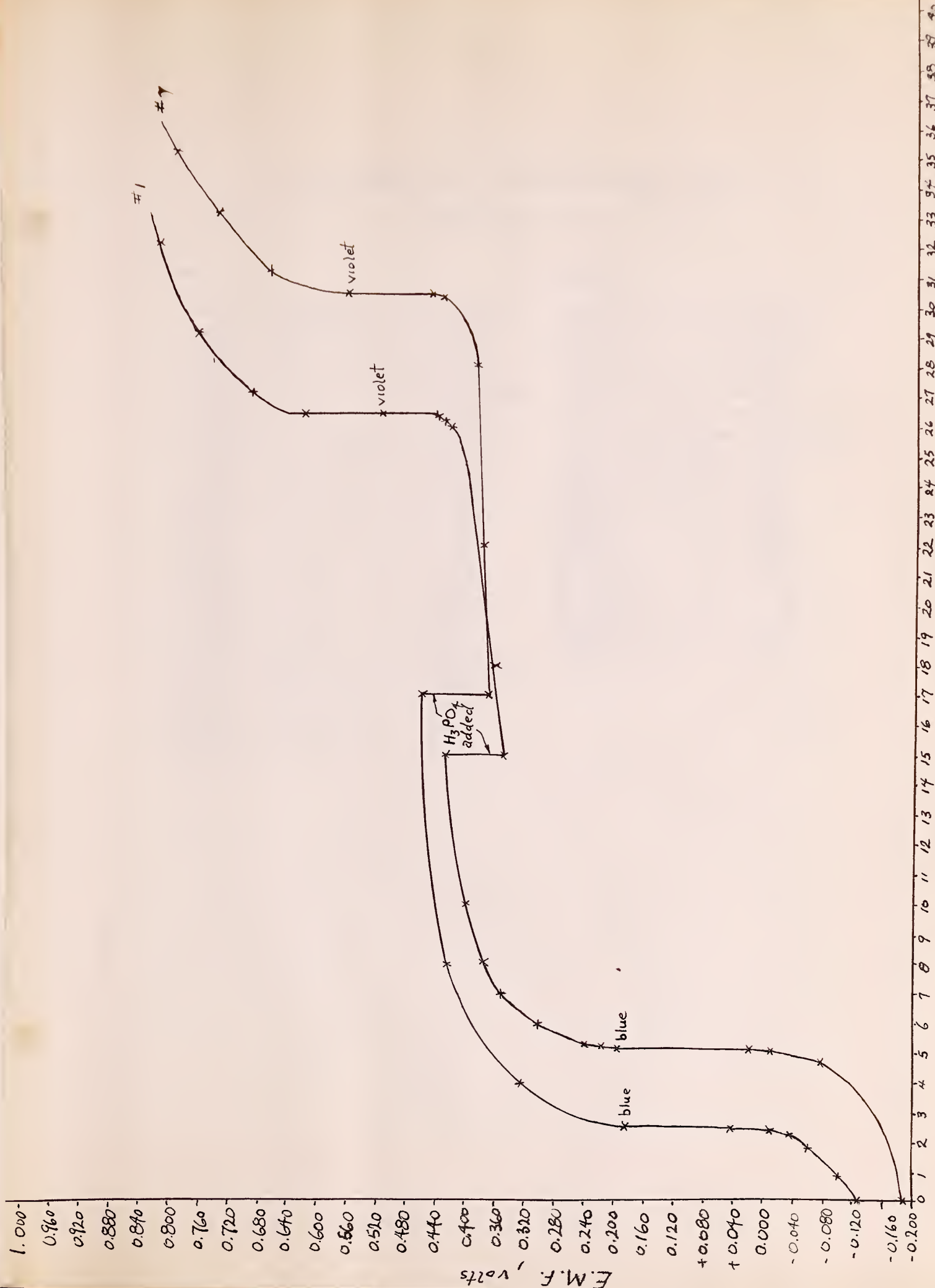
Standardization of potassium dichromate against iron wire (99.8% pure), using the Zimmermann-Reinhardt method.

no.	ml. of $K_2Cr_2O_7$	wt. of iron wire	normality of $K_2Cr_2O_7$
1	62.71	0.6185	0.1766
2	63.35	0.6244	0.1762
3	62.70	0.6180	0.1765
Average			0.1764

TABLE XX

Determination of iron in United States Bureau of Standards, sample no. 26, using standard potassium dichromate, titanium hydride, and indigo disulfonate.

no.	ml. of 0.1764 N $K_2Cr_2O_7$	wt. of iron sample no. 26	per cent of iron
1*	21.13	0.3548	58.66
2	14.45	0.2427	58.65
3	37.68	0.6330	58.63
4	15.93	0.2681	58.52
5	20.65	0.3469	58.64
6	26.00	0.4373	58.56
7*	27.60	0.4633	58.68
8	28.38	0.4770	58.61
9	23.85	0.4010	58.59
Average			58.62
United States Bureau of Standards result - 58.62			



ml. of 0.1706N K₂Cr₂O₇ solution

POTENTIOMETRIC DATA FOR DETERMINATIONS SHOWN IN

TABLE XX AND GRAPH 5

Sample #1		Sample #7
0.00 ml. $K_2Cr_2O_7$	-0.190 v.	0.00.....-0.110
4.90.....	-0.080	1.00.....-0.105
5.15.....	-0.010	2.00.....-0.060
5.18.....	+0.023	2.40.....-0.040
5.20.....	+0.195 blue	2.55.....-0.010
5.25.....	0.215	2.65.....+0.040
5.30.....	0.240	2.68.....0.185 blue
6.00.....	0.305	4.00.....0.325
7.00.....	0.350	8.00.....0.425
8.00.....	0.375	17.00.....0.460
10.00.....	0.400	17.00.....0.365
15.00.....	0.430	28.00.....0.385
15.00.....	0.352	30.20.....0.430
18.00.....	0.359	30.25.....0.451
22.00.....	0.378	30.28.....0.560 red
26.00.....	0.424	31.00.....0.667
26.20.....	0.433	33.00.....0.740
26.30.....	0.440	35.00.....0.790
33.00.....	0.516 red	
35.00.....	0.618	
27.00.....	0.689	
29.00.....	0.760	
32.00.....	0.813	

TABLE XXI

Determination of iron in United States Bureau of Standards sample no. 26, using 0.1764 N potassium dichromate and the Zimmermann-Reinhardt method.

no.	ml. of 0.1764 N $K_2Cr_2O_7$	wt. of iron sample no. 26	per cent of iron
1	40.93	0.6871	58.68
2	29.85	0.5016	58.62
3	29.10	0.4891	58.61
Average			58.63

TABLE XXII

Determination of iron in United States Bureau of Standards sample no. 26, using titanium hydride, ceric sulfate, and indigo disulfonate.

no.	ml. of 0.08606 N $Ce(SO_4)_2$	wt. of iron sample no. 26	per cent of iron
1	40.60	0.3290	58.65
2	31.07	0.2520	58.60
3	24.00	0.1944	58.68
4	29.10	0.2359	58.63
5	42.59	0.3454	58.61
6	42.13	0.3412	58.67
7	36.40	0.2950	58.65
8	39.75	0.3221	58.66
9	29.50	0.2393	58.59
10	35.20	0.2851	58.68
Average			58.64

United States Bureau of Standards result - 58.62

TABLE XXIII

Standardization of $Ce(SO_4)_2$ against pure As_2O_3

no.	ml. of $Ce(SO_4)_2$	wt. of As_2O_3	normality of $Ce(SO_4)_2$
1	53.52	0.2253	0.08512
2	25.45	0.1070	0.08506
3	29.60	0.1246	0.08512
4	38.50	0.1620	0.08508
5	19.40	0.0817	0.08515
Average			0.08511

TABLE XXIV

Determination of iron in United States Bureau of Standards sample no. 26, using potassium permanganate, titanium hydride, and indigo disulfonate.

no.	ml. of KMnO_4 (0.1210 N)	wt. of iron sample no. 26	per cent of iron
1	33.93	0.3910	58.63
2	35.00	0.4038	58.56
3	20.65	0.2381	58.60
4	39.78	0.4584	58.63
5	26.35	0.3035	58.65
6	23.90	0.2758	58.55
7	33.03	0.3806	58.63
8	27.60	0.3180	58.64
9	27.20	0.3134	58.64
10	41.30	0.4760	58.62
11	22.30	0.2573	58.55
Average			58.61
United States Bureau of Standards result - 58.62			

TABLE XXV

Standardization of KMnO_4 with $\text{Na}_2\text{C}_2\text{O}_4$ (100.01% pure)

no.	ml. of KMnO_4	wt. of sodium oxalate	normality of KMnO_4
1	30.28	0.2454	0.1209
2	35.50	0.2880	0.1211
3	36.57	0.2965	0.1210
Average			0.1210

The results of the preceding tables show that the new determination using titanium hydride and an indigo sulfonate indicator is just as accurate as the classical Zimmerman-Reinhardt procedure, and far less involved and time-consuming. Using the results we have obtained, we may now give two new analytical procedures, as follows:

1. The determination of iron by using titanium hydride as a new reducing agent.
2. The simultaneous determination of iron and titanium with the same standard solution.

Procedure 1:

The iron sample is dissolved in concentrated hydrochloric acid, or by any of the usual methods. Stannous chloride, however, cannot be added to help the iron solution by converting ferric to ferrous iron. A little sulfurous acid might be added instead, if this is necessary. When the iron is in solution, the hydrochloric acid or nitric acid is removed by adding 10 ml. of sulphuric acid and bringing to sulphur trioxide fumes. The solution is then diluted with water (care being taken to avoid splattering) until the sulphuric acid concentration is approximately 10 N. Now approximately 25 mgs. of titanium hydride per milli-equivalent of iron is added to the solution, and is spread over the bottom of the beaker by a few gentle swirls. The solution is then heated until a clear blue or purple coloration is obtained. If the hydrogen is expelled too rapidly, the solution must be heated more slowly. It should not be necessary to boil the sulphuric acid solution unless too much water is added; then, large quantities of water must be expelled before a 12 N concentration and 120-130° temperature are reached. If the hydride is added to a hot 12 N sulfuric acid solution, the hydrogen is expelled very rapidly, and more hydride is required for the reduction. Complete reduction is indicated by the presence of purple titanous ions.



(Caution: the titanium hydride should not be allowed to drop on top of a hot plate or asbestos pad, since the hydrogen will gradually be expelled and the titanium metal will ignite with the evolution of great quantities of heat.) When a clear purple solution is obtained, 5-8 drops of a 1% indigo disulfonate solution is added. The colorless leuco- compound is formed in the presence of titanous ions. The solution may now be titrated with either standard permanganate, ceric sulfate, or dichromate solutions, with slight variations.

These are as follows:

A. Permanganate

The sulphuric acid concentration should be 1 M or less. If care is taken, 10 cc. or less of the sulphuric acid can be used in the reduction, and the solution is then diluted to about 400 ml. and titrated. A deep blue color is formed at the first titanium end point. With further addition of permanganate, the blue coloration gradually fades. It is completely destroyed before the iron end point. If so desired, 5 cc. of phosphoric acid may be added (near the second end point), and the permanganate end point will be improved by the removal of the yellow ferric coloration. The indicator blank is a drop or less.



B. Ceric sulfate

The sulphuric acid concentration should be 3-6 N. Osmic acid (3 drops of 1% sulphuric acid solution) is added as catalyst. Indigo disulfonate is used as before, and orthophenthroline ferrous complex for the iron end point. The indicator blank is a drop or less. The indigo is destroyed as the iron end point is approached.

C. Dichromate

The sulphuric acid concentration should be 5-7 N. Tetrasulfonate of indigo may be used if the disulfonate is obscured by the chromic ions. The indigo indicators are not completely destroyed before the iron end point is reached. The sodium diphenylamine sulfonate indicator, however, can be seen in good light. Ten cc. of phosphoric acid is added near the iron end point to prevent the sodium diphenylamine sulfonate from changing color too soon.

Procedure 2:

In the light of the work discussed in this report and the work of Subbaraman and Krishnaswami discussed on page 11, a procedure may be given for the simultaneous determination of titanium and iron, using one standard solution. This solution may be permanganate, ceric sulfate, or dichromate. The method of application would be identical with that given in Procedure 1. A mixture of titanous and ferric ions could be reduced in any suitable reductor, such as the Jones reductor



(see TABLE I, page 5). To obtain accurate results for titanium, the loss due to air oxidation would have to be prevented. This could be done by titrating over a nitrogen or carbon dioxide atmosphere. This is not necessary. Using the modification of Subbaranan and Krishnaswami, at least three samples should be run. In the first, a slightly low value for titanium would be obtained. In the last two samples, the reduced solution would be collected in a volume of standard solution 0.2 - 0.3 ml. less than required to oxidize the titanous ions. This volume would be estimated from the first titration. The reduction would be immediately completed, using indigo di- or tetrasulfonate, as in Procedure 1, followed by the reduction of iron, using the same standard solution. From the two end points, we would know the volumes of standard permanganate, ceric, or dichromate solution corresponding to the titanium and to the iron contents.

SUMMARY

The results obtained in this research show conclusively that titanium hydride can be used as a reducing agent, in place of stannous chloride, in the determination of iron. Also, indigo disulfonate or tetrasulfonate can be used to indicate the titanium end point with very great accuracy. By using the method of guide samples, as developed by Subbaraman and Krishnaswami, whose work was discussed on pages 11-13 of this report, titanium and iron could be determined simultaneously in the same solution by using either permanganate, cerium, or dichromate standard solutions.

The aeration procedures, as described by Trout and Pearson (see page 9 and 10) and H. Axt and H. Le Roy (see page 15), would not be necessary, using the methods described herein. Likewise, the procedure proposed by Isibasi and Kadoya (see pages 16 and 17), whereby a mixture of titanium and iron is determined in two steps, becomes unnecessary. The Jones reductor may be used in the reduction of ore and soil samples of iron which contain appreciable amounts of titanium, since the latter may be titrated simultaneously with iron.

Titanium hydride has several advantages over stannous chloride as a reducing agent for iron. First, the determin-

The first part of the paper discusses the importance of the study and the objectives of the research. It also provides a brief overview of the methodology used in the study. The second part of the paper presents the results of the study and discusses the implications of the findings. The third part of the paper concludes the study and provides some final thoughts on the research.

The study was conducted using a qualitative research approach. The data was collected through interviews with participants who were selected through purposive sampling. The interviews were conducted in a semi-structured format, allowing the researcher to explore the participants' experiences and perspectives in depth. The data was then analyzed using thematic analysis to identify the key themes and patterns in the data.

The findings of the study indicate that there are several factors that influence the participants' experiences. These factors include the participants' social and cultural background, their personal experiences, and the context in which they are operating. The study also found that the participants' experiences are shaped by the interactions between these factors. The implications of the findings suggest that there is a need for further research to explore these factors and their interactions in more detail.

In conclusion, the study has provided valuable insights into the participants' experiences and the factors that influence them. The findings have important implications for the field and suggest that there is a need for further research to explore these factors and their interactions in more detail.

ation can be made without the presence of chloride ion. Second, precautions taken against an excess of stannous chloride are unnecessary in the use of titanium hydride. Third, the purple coloration of the titanous ions indicates the completion of the iron reduction. Fourth, a special process for the destruction of excess titanous ions is not necessary, since the latter may be titrated with the same standard solution as used for iron. Fifth, only very small amounts of the hydride (25 mgs./1 milli-equivalent of iron) are needed to reduce iron. Sixth, the time required for reduction is very short (three to five minutes).

BIBLIOGRAPHY

Brensecke, E., K. Fajans, H. H. Farman, R. Lang, and H. Stann, Newer Methods of Volumetric Analysis, translated by R. E. Oesper. D. Van Nostrand Company, 1938.

Clark, W. M., The Determination of Hydrogen Ions, third edition. Williams and Wilkins, 1928.

Ephraim, Fritz, Inorganic Chemistry, translated and revised by P. C. L. Thorne and A. M. Ward, third English edition. Nordeman Publishing Company, 1939.

Getman, Frederick H., Outlines of Theoretical Chemistry, sixth edition by Farrington Daniels. John Wiley and Sons, 1940.

Gooch, F. A., Methods in Chemical Analysis. John Wiley and Sons, 1929.

Hillebrand, W. F. and G. E. F. Lundell, Applied Inorganic Analysis. John Wiley and Sons, 1929.

Johnson, C. M., Rapid Methods for the Chemical Analysis of Special Steels, third edition. John Wiley and Sons, 1920.

Knecht, E. and E. Hibbert, New Reduction Methods in Volumetric Analysis. Longmans, Green, and Company, 1918 and 1925.

Kolthoff, I. M., Volumetric Analysis, two volumes, first edition, translated by N. H. Furman. John Wiley and Sons, 1928, 1929.

Kolthoff, I. M. and N. H. Furman, Potentiometric Titrations, second edition. John Wiley and Sons, 1931.

Kolthoff, I. M. and E. B. Sandell, Textbook of Quantitative Inorganic Analysis. Macmillan Company, 1936.



Lundell, G. E. F. and J. I. Hoffman, Outlines of Methods of Chemical Analysis. John Wiley and Sons, 1934.

Michaelis, L., Hydrogen-ion Concentration, translated by W. A. Perlzweig. Williams and Williams, 1926.

Mitchell, A. D. and A. M. Ward, Modern Methods in Quantitative Chemical Analysis. Longmans, Green, and Company, 1932.

Scott's Standard Methods of Chemical Analysis, fifth edition, two volumes, edited by H. H. Furman. D. Van Nostrand Company, 1939.

Smith, Frederick G., Ceric Sulfate, Volume I, second ed. G. F. Smith Chemical Company, July, 1933.

Sutton, F., Volumetric Analysis, eleventh edition, revised by W. L. Sutton and A. E. Johnson. P. Blakiston's Son and Company, 1931.

Treadwell, F. P., Analytical Chemistry, Volume II, Quantitative, translated by W. T. Hall. John Wiley and Sons, 1919.

Washington, The Chemical Analysis of Rocks.

Willard, Hobart H. and W. H. Furman, Elementary Quantitative Analysis. D. Van Nostrand Company, 1941.

Yoe, J. E., Chemical Principles. John Wiley and Sons, 1937.

United States Government Patents:

Number 2,038,402. April 21, 1936.

Number 2,163,224. June 20, 1939.

Number 2,163,185. August 1, 1939.

Clark, W. M., Studies on Oxidation-Reduction, U. S. P. H. Dept., Reprint No. 843, pages 1569-1718. 1923.

Hillebrand, W. F., Analysis of Silicate and Carbonate Rocks, page 166, Bulletin 700, United States Geological Survey. Government Printing Office, 1919.

Jameson, G. B., Volumetric Iodate Methods, Chemical Catalog Company, 1928.

Moore, R. B. et al., Analytical Methods for Certain Metals, Bulletin 213. United States Bureau of Mines, 1923.

Periodicals

Ast, M. and A. Le Roy, "Aeration Procedure for Titanium," L'ingénieur chimiste, Volume 24, p. 2-31. 1940.

Bradbury and Edwards, "Direct Method for Iron, Using Mercurous Nitrate," J. of Soc. of Chemical Industries, Transactions, Volume 59, p. 95-8. 1940.

Cole, S. S. and C. A. Kurnias, "Determination of Iron, Vanadium, and Titanium in the Same Solution," Bull. Am. Ceramic Soc., Volume 20, p. 329-31. 1941.

Ferrey, "Discussion of the Iodometric Method for Iron," Quart. J. of Pharmacy, Volume 3, p. 471. 1930.

Fresenius, "Use of Iodine to Determine Excess Stannous Chloride in Determination of Iron," Zeitschrift für Analytische Chemie, Volume 1, p. 26. 1862.

Gooch and Newton, "Elimination of Titanous Ions," Amer. J. of Science, Volume 23. 1907.

Heisig, "Potassium Iodate in the Volumetric Determination of Iron," J. Am. Chem. Soc., Volume 59, p. 1678. 1928.

Isibasi and Kadoya, "Determination of a mixture of Iron and Titanium," J. Chem. Soc. of Japan, Volume 62, p. 316-318. 1941.

Lundell and Knowles, "Quantitative Determination of a Mixture of Iron and Titanium," J. Am. Chem. Soc., Volume 43, p. 1563. 1921.

Manchot and Oberhauser, "Bromometric Method for Iron," Z. Analytische Chemie, Volume 57, p. 196. 1926.

Mohr, "Volumetric Method for Iron, Using Potassium Iodide," Annalen, Volume 105. 1858.

Nicholson, "Short Volumetric Method for Iron and Titanium," Bull. Am. Ceramic Soc., Volume 20, p. 331-4. 1941.

Novakovskii and Tsionskaya, "Determination of Titanium in the Presence of Iron, Zavodskaya Laboratoriya, Volume 9, No. 1, p. 103-4. 1940.

Ryabchikov and V. G. Sil'nikenko, "Potentiometric Determination of Iron," J. of Applied Chem., (U. S. S. R.), Volume 12. 1907-1911. In French, 1911.

Subbaraman and Krishnaswami, "Determination of Iron and Titanium in Ilmenite," Proceedings of Indian Academy of Science, 11A, p. 106-115. 1940.

Thornton and Rosenau, "Aeration Procedure for the Elimination of Titanium," J. Am. Chem. Soc., Volume 57, p. 619-621. 1935.

Titus, A. C. and C. W. Sill, "Potassium Dichromate in the Determination of Iron, Using Siliconomolybdic Acid Indicator Before the Volumetric Oxidation of Iron," Ind. and Eng. Chem., Anal. Ed., Volume 13, p. 416-18. 1941.

Titus, A. C. and C. W. Sill, "Ceric Sulfate in the Determination of Iron, Using Siliconomolybdic Acid Indicator Before the Volumetric Oxidation of Iron," Ind. and Eng. Chem., Anal. Ed., Volume 14, p. 121. 1942.

Walden, Harlett, and Edmonds, "Reduction of Iron by Use of a Silver Reductor," J. Am. Chem. Soc., Volume 56, p. 330. 1934.

Zeiverts, "Metal-Hydrogen Systems," (Summary), Z. Angewandte Chemie, Volume 21, p. 37. 1929.

